MOLECULAR ORBITAL INVESTIGATIONS OF METAL-OXO CATALYZED OXIDATIONS

BY

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1990

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This thesis is dedicated to the memory of my father,
Michael V. Cundari Sr. (1925-1988), whose lessons about
hard work and perseverance has more to do
with the completion of this dissertation
than any of the chemistry I ever learned.

ACKNOWLEDGMENTS

No one lives life, or does research, in a vacuum. The amount of people who must be thanked is enormous. Family and friends are the most obvious choice. Even for an anti-social beast such as myself, they are too numerous to mention. They know who they are; my life, my research and this dissertation have profited from knowing them. Colleagues, instructors and mentors are gratefully acknowledged for the intellectual stimulation of many fruitful discussions. I owe a very special debt of gratitude to my research advisor, Professor Russell S. Drago, for putting up with my harassment and giving it back. Although it is unfair to single out a single member from the rest of my Doctoral Committee, it would be even more unfair not to acknowledge the contribution of Professor Michael C. Zerner to my chemical education. His seemingly boundless energy and enthusiasm, as well as encouragement, has provided much motivation. I would like to thank the rest of the Department of Chemistry at the University of Florida (in particular, the Division of Inorganic Chemistry, i.e. the best, most happening division on campus!), for providing a great place to live, work and play. Those who are connected with the running and maintaining of the microVAX (upon which

the majority of the research presented here was carried out), i.e. Steve Cato, Erik Deumens and the rest of QTP, etc. are acknowledged.

Some specific acknowledgements for the work contained herein are necessary. Much of the work was supported in part by grants from the National Science Foundation and the United States Army. For our work on epoxidations, we gratefully acknowledge helpful discussions with K. F. Purcell (Kansas State University) and a generous grant of computer time by A. S. Goldstein and G. C. Martin. The epoxidation work is based on a talk delivered by the author at the 197th National Meeting of the American Chemical Society in Dallas. The author wishes to thank the organizer of the Symposium on Oxygen and Related Group Transfers, J. T. Groves (Princeton), for organizing a wonderful symposium and to the other participants for many stimulating discussions. The work on alcohol oxidation was presented at the 29th Sanibel Symposium organized by the Quantum Theory Project of the University of Florida. The organizers of the Sanibel Symposium are thanked for their hospitality. The help of Greg Harris in preparing the section on alcohol oxidations is gratefully acknowledged. Gilda Loew (Molecular Research Institute) was kind enough to supply reprints of her work (References 4c and 4d).

From the obvious we must go to the obscure. I would be remiss in concluding this acknowledgement section without

professing the great sense of gratitude I feel toward those who have gone before me, i.e. Lewis, Pauling, Mulliken, Hund, HÜckel and the myriad of other who have taken this still relatively new quantum theory and wrested it from those who would turn theoretical chemistry into an exercise in "number crunching." I have always believed, still believe, and hopefully will always believe that the purpose of theoretical chemistry is to illuminate, stimulate and suggest to our brethren, the experimental chemist, the what, why, where and how of this great science - chemistry.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy

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August, 1990

Chairman: Professor Russell S. Drago
Major Department: Chemistry

Molecular orbital analyses of oxidations by a six-coordinate, Ru(IV)-oxo complex (cis-[Ru(HN=CH-HC=NH)$_2$(NH_3)(O)]$^{2+}$) are combined with experimental data and basic electronic structural arguments in an effort to understand the nature of the chemical bond in the systems studied. An analysis of the pathways and intermediates for the epoxidation of olefins using a six-coordinate, Ru(IV)-oxo model complex is presented. As in the overwhelming majority of calculations described herein, INDO/1 calculations were used. As with the more familiar organic analogues, concerted [1+2] and [2+2] cyclo-additions lead to unfavorable orbital interactions. A non-concerted [1+2] process is preferred. The initial interaction between substrate and catalyst in the oxidation of alcohols by the

same Ru(IV)-oxo complex is studied using the INDO/1 method. Activation of the C-H bond of the alcohol by the oxo oxygen of the Ru(IV)-oxo complex is compared and found to be competitive with inner-sphere coordination shell expansion of the Ru-oxo catalyst. The preferred pathway combines aspects of both proposals, i.e. C-H-Oxo activation and coordination to the metal. The subsequent conversion of the coordinated methanol to carbonyl products is also discussed. An INDO/1 investigation of the oxidation of organic sulfides by the Ru(IV)-oxo complex is presented. Two distinct reaction pathways were considered: oxygen atom transfer to the sulfide and pre-coordination of the sulfide to the metal. Oxygen atom transfer was found to be the most favorable pathway in agreement with experimental evidence. The INDO/1 model is employed to analyze the reaction between olefins and cis- and trans- Ru(VI)-dioxo complexes. The differences in reactivity of olefins with the cis- and trans-Ru(VI)-dioxo complexes arise from different preferred pathways: a non-concerted [1+2] pathway for the trans isomer and a concerted [3+2] pathway for the cis isomer.

CHAPTER 1
INTRODUCTION

The oxidation of organic substrates catalyzed by transition metal complexes is an area of great scientific interest.[1,2,3] Biological[4,5] and industrial[6,7] processes have spurred this great interest. One example is the oxidation of organic species to less toxic, more water soluble products by cytochromes P-450,[8] with their iron-porphyrin active site.[9] Another example is the conversion of cyclohexane to cyclohexanol and cyclohexanone (which are subsequently converted to adipic acid,[10] an important precursor in the manufacture of Nylon) catalyzed by a homogeneous Co(II) catalyst.

Two distinct transition metal oxidation systems are the η^2 - peroxide[11,12] and the metal-oxo.[13] Much experimental and theoretical work has gone into understanding these oxidants. Group VIB η^2 -peroxides have received their greatest use as catalysts for the epoxidation of olefins.[14,15] Two alternate proposals have dominated much of the discussion as to the mechanism for the epoxidation of olefins by the η^2 peroxo complexes. The so-called Mimoun[14] mechanism involves the pre-coordination of the olefin to the metal followed by a [1+3] dipolar cycloaddition to an MO_2

fragment to yield the proposed, five-membered ring intermediate - the peroxometallocycle. This intermediate then undergoes an [1+3] dipolar cycloreversion to produce the epoxide product. In the Sharpless[15] variation there is direct nucleophilic attack of the olefin on one of the oxygen atoms of the peroxide moiety. Electronic rearrangement yields the epoxide product by what amounts to direct oxygen atom transfer. In both cases the other oxygen of the peroxide unit becomes an oxo oxygen. An external oxidant (such as HOOH or an organic hydroperoxide, ROOH) is necessary to regenerate the active peroxo species. A theoretical analysis by Jorgensen and Hoffmann[16] using the Extended HÜckel method[17-19] suggests a mechanism which is a hybrid of the Sharpless and Mimoun formulations. There is activation of the olefin by coordination to the electron-deficient, high-valent metal followed by migration of the olefin toward a peroxide oxygen to form a species similar to the Sharpless intermediate. Purcell[20] considered the energetics for decomposition of the most widely proposed intermediate in epoxidation of olefins by an n^2-peroxo complex, i.e. the peroxometallocycle (a five-membered M-O-O-C-C ring), to an epoxide for both Mo(VI) and a Rh(III) systems. Once again, Extended HÜckel calculations were used to delineate the pertinent orbital changes and energetics associated with the reaction.[20]

Another prevalent substrate for oxidations by η^2 peroxides have been organic sulfides, R_2S. DiFuria and co-workers[21] have shown $MoO(O_2)_2L$ (L = basic ligand, e.g. $PO(NMe_2)_3$) complexes to be effective sulfide oxidation catalysts. The products are mainly sulfoxide, R_2SO, and sulfone, R_2SO_2. Research conducted in our own laboratories[22] has shown metal-acetylacetonoate complexes ($Mo(O)_2$-$(acac)_2$ and $VO(acac)_2$) to be potent sulfide oxidation systems in the presence of $(CH_3)_3COOH$ in acetonitrile solution. The most plausible active species is the η^2-peroxide. Drago and co-workers[23] have also shown $MoO(O_2)(H_2O)(C_5H_3N(CO_2)_2)$ to be an effective sulfide oxidation catalyst.

The current interest in metal-oxo chemistry was initiated by the discovery of Groves and co-workers[24] that iodosyl benzene (C_6H_5-I-O) and Fe(III)tetraphenyl porphyrin chloride could mimic the reactivity of the class of enzymes cytochromes P-450 and molecular oxygen. Cytochromes P-450 are a family of monooxygenases responsible for the oxidation of lipophilic substrates. The active species is thought to be a ferryl heme complex. Groves and co-workers have carried out a detailed experimental characterization of the iron and related P-450 models.[25-30] Since then, many different oxygen atom transfer reagents (such as C_6F_5-I-O[31], Cl-O[-32,33], R_3N-O[34,35], etc) and metal species have been investigated.[36-42] Metal-oxo reagents have been used to

oxidize a wide range of substrates: olefins to epoxides,[43-52] alcohols to ketones and aldehydes[53], sulfides to sulfoxides and sulfones,[54] N-alkyl amines to less substituted amines,[55] hydrocarbons to alcohols,[56-61] and others.[62]

Theoretical research into the pathways and intermediates used in metal-oxo mediated oxidations has been very profitable. Using Extended HÜckel MO calculations Jorgensen[63] has investigated the conversion of an Fe-oxo porphyrin species (Fe[porphyrin](O)(H_2O)) to an N-oxo precursor. The proposal of the N-oxo (the N is from one of the nitrogen ligands, i. e. the pyrrole unit of the porphyrin) as the active species in the oxidation of organic substrates by P-450 models was derived from the work by Bruice and his collaborators[34,35] which showed that nitrogen-oxides (e.g. pyridine N-oxide or morpholine N-oxide) could act as oxygen atom transfer reagents. Jorgensen's results indicate that this perturbation is possible. Jorgensen proceeds to analyze the interaction between the N-oxo species and ethylene leading to epoxide formation. Strich and Veillard[64] have used ab-initio wavefunctions to study this isomerization for a similar species - Fe[porphyrin](O)(py). Their results indicate that this isomerization is quite unfavorable with the N-oxo intermediate being approximately 100 kcal mol^{-1} higher in energy than the ground state Fe-oxo isomer.

Goddard and Carter[65] have studied metal-oxo diatomic systems using Generalized Valence Bond Theory[66-68] and then subsequently[69] have shown how the properties of the isolated metal reactive site could be transferred to a larger, coordinatively saturated complex which contained this same fragment. Rappé and Goddard[70,71] have looked at the proposed intermediates and transition states for the oxidation of olefins with Group VIB metal-oxo reagents (e.g. MoO_2Cl_2 and CrO_2Cl_2) using GVB calculations. Their analysis indicates that a four-membered M-O-C-C ring structure, i.e. a oxometallocycle, is the most favorable intermediate and that the driving force for the reaction (to produce epoxide) is the strengthening of the second metal-oxygen bond from an approximate double bond to a triple bond as the first oxygen atom is being transferred.[70] Rappé and Goddard also studied models for molybdenyl and chromyl species supported on inorganic oxides (alumina, silica, etc.).[71] Goddard carried out a detailed analysis of the ground and excited states of NiO and commented at length as to the similarity of this species with molecular oxygen with respect to the low energy excited states which are generated by electron correlation within the Ni $d\pi$ - O $p\pi$ MOs.[72] Bauschlicher and co-workers have compared PdO and NiO, MoO and CrO, and CuO and AgO with the aim of delineating the crucial differences between first and second transition series with respect to their electronic structure and chemical bonding.[73] Krauss and

Stevens have employed pseudo-potential methods to compare RuO and FeO.[74] In both cases the ground state possesses a dioxygen-like $\pi^4\pi^{*2}$ electronic configuration. Bagus has investigated FeO using all-electron ab-initio calculations.[75] He concludes on the basis of his calculations that the ground state of FeO is not $^5\Sigma^+$ as has been proposed.[75] Goddard and Carter have utilized the GVB method to study typical early (VO^+) and late (RuO^+) transition metal oxo species.[65] Their results indicate that the early transition metal oxo species are similar to carbon monoxide, i.e. a strong, approximately triple bond, and that the later transition metal oxo complexes are more like dioxygen, i.e. covalent π system. This rationalizes why the early transition metal-oxo systems, e.g. vanadyl and molybdenyl, do not readily engage in direct oxygen atom transfer while later transition metal-oxo systems, e.g. Ru-oxo, can. Loew and others [76,77,78] have employed semi-empirical MO calculations (of the NDO type[79-84]) in their studies. Much of the work of Loew and her co-workers has been concerned with the electronic structure of iron complexes which are germane to P-450 model systems. Loew has, however, published an MO analysis of the oxidation of aromatic hydrocarbons,[85a] the conversion of ethylene and methane to ethylene oxide and methanol, respectively,[85b] and the oxidation of propylene (allylic oxidation versus epoxidation).[85b] The P-450 model studied in these papers

was triplet oxygen (^3P). These studies show that O (^3P) is a good qualitative model for the active oxidizing species in cytochrome P-450. Using O (^3P) to model the active species in cytochromes P-450 neglects effects brought about by the metal and ligands.[85c] Blyholder, Head and Ruette have analyzed Fe-dioxo species using a semi-empirical MINDO model and have shown it to describe the chemistry of these species quite well.[86] Their main goal was to understand the interaction between molecular oxygen and atomic iron. Zerner and co-workers[87,88] (using the spectroscopic, semi-empirical INDO/1 model developed in his laboratories) and Yamamoto and co-workers[89] (using ab-initio calculations) have presented detailed analyses of the ground and low energy excited states of the iron-porphyrin reactants (Fe(II)[porphyrin][87] and Fe(III)[porphyrin]Cl[88]) and a model for the proposed active species, Fe(IV)O(porphyrin)(py), respectively. The ab-initio CASSCF (complete active space, self-consistent field) study by Yamamoto et al. [89] has shown that for the Fe[porphyrin](py)(O) model system that the ground state is largely ionic, Fe^{+4}-O^{-2}, with this configuration or "resonance structure" comprising over 80% of the ground state wavefunction. The greater covalency of comparable second transition series bonds versus those for the first transition series (i.e. the metals belong to the same group of the Periodic Table) has been appreciated by Bauschlicher and his group.[73,90] The study of Bauschlicher

et al. deserves special mention since it is the only detailed comparison of the nature of the chemical bond for analogous first and second row transition metal species that has been published. The Ru-oxo bond is much more covalent than the Fe-oxo bond as noted by Goddard and Carter.[65]

Theoretical research on the nature of the bonding in the reacting systems has been sparse.[91-93] Sevin has used Extended HÜckel wavefunctions as a starting point for the construction of Valence Bond (VB) wavefunctions. The reaction of interest was the Fe-oxo mediated oxidation of ethylene to ethylene oxide. The model complex studied was FeH_4O^{2-}.[92,93] Sevin concludes that the preferred pathway is a non-concerted formation of the bound epoxide. This study suffers in two respects - the use of Extended HÜckel to describe a polar system and the modelling of a porphyrin by four hydrides. Yamaguchi and co-workers have looked at the interaction of ethylene with various diatomic metal-oxides.[91] Their results show that the preferred pathway depends strongly on the particular metal. As mentioned previously, the ligands play an essential role.

CHAPTER 2
EPOXIDATIONS

Introduction

The mechanism of epoxidation by transition metal-oxo systems has been intensively studied by experimentalists, particularly for iron-oxo as it is the proposed active species in cytochrome P-450 catalyzed oxidations.[24] The approach taken in the present work is to use INDO/1 calculations to explore the potential energy surface (PES) for the interaction of ethylene with the metal-oxo reactant and analyze the results using the language of the Woodward-Hoffmann rules.[94] A Ru(IV)-oxo complex, Figure 2-1, was chosen since it is a well characterized complex[43] which is similar to the biologically significant Fe-oxo species.[24]

Calculations

The calculations were carried out on a microVAX using a semi-empirical INDO/1 program written by M. C. Zerner and his group. The UHF formalism of Pople and Nesbet[95] was used since most of the species involved are open-shell molecules. To reduce the overall basis set size, and computer time, glyoxal diimine was used in the calculation to model the experimentally employed nitrogen ligands, Figure 2-1.

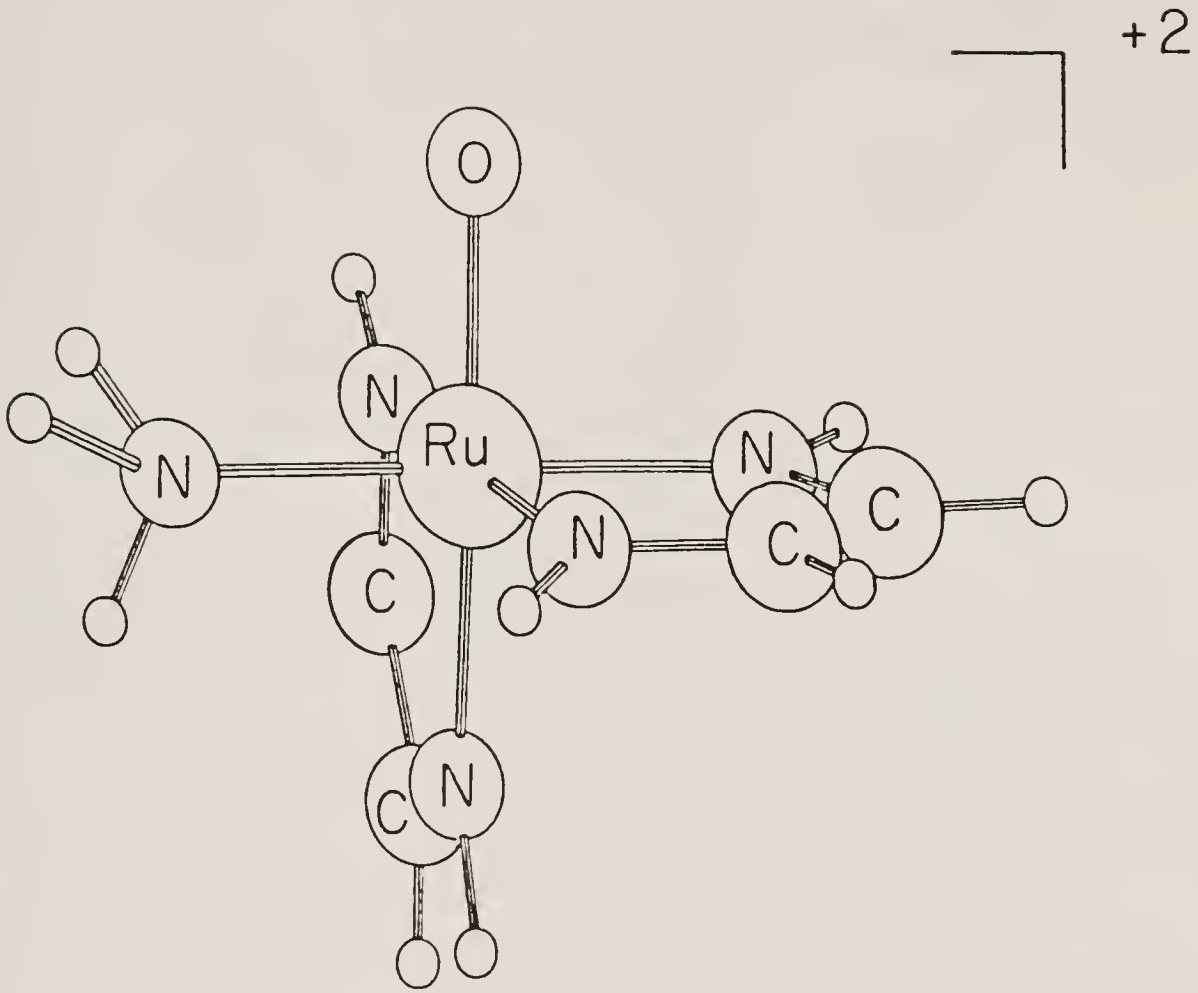


Figure 2-1: Geometry of the Ru-oxo model complex upon which the calculations were performed.

Bipyridine parameters (bond lengths and angles) were used for glyoxal diimine[96] and free ammonia values[96] for the ammonia ligand in the model complex, Figure 2-1. Gradient driven geometry optimizations[97] were carried out on various Ru-oxo/ethylene species to yield stationary points on the PES. The M-L bond lengths were obtained by INDO/1 geometry optimization (Ru-O = 1.96Å, Ru-N = 2.06Å) and agree well with the experimental values.[98] Convergence to a minimum on the PES was assumed when the gradient was less than 5.0×10^{-3} Hartrees/Bohr.

The atomic bond index used in the MO analysis is defined as

$$B_{AB} = \sum_{u}^{\text{on A}} \sum_{v}^{\text{on B}} P_{uv} * P_{vu} \qquad (1)$$

where the summation is over all atomic orbitals $|\chi_u\rangle$ and $|\chi_v\rangle$ on atoms A and B, respectively and P_{uv} is the bond order or density matrix element between $|\chi_u\rangle$ and $|\chi_v\rangle$. The atomic bond index yields a value of 1 for a single bond, 2 for a double bond, etc. P_{uv} is defined as

$$P_{uv} = \sum_{i}^{\text{occ.}} c_{ui}\, c_{vi} \qquad (2)$$

where c_{ui} and c_{vi} are the AO coefficients of $|\chi_u\rangle$ and $|\chi_v\rangle$ in MO $|\Psi_i\rangle$ using the LCAO-MO approximation.

Results and Discussion

Electronic Structure of the RuN_5O^{2+} Complex

The frontier MO diagram for the d^4 RuN_5O^{2+} complex is that of a octahedron (i.e. energy(t_{2g}) < energy(e_g^*)) with the d_{xz} and d_{yz} components of the t_{2g} being perturbed to higher energy by antibonding mixing with the lower energy O $2p\pi$ AOs. The RuN_5O^{2+} complex is similar to oxygen in that it contains a filled Ru $d\pi$ - O $p\pi$ bonding level and a half-filled Ru $d\pi$ - O $p\pi$ antibonding level. The π and the π^* are comprised largely of Ru $d\pi$ and O $p\pi$ AOs. As with O_2 there are low energy singlet and triplet states.[99] The ground state triplet ($\pi_1^*\alpha$ $\pi_2^*\alpha$) is calculated to be ≈1eV below the lowest energy singlet state ($\pi_1^*\alpha$ $\pi_1^*\beta$). Note that the formal oxidation state on the metal is +4, yielding a d^4 metal.

Formation of an N-oxo Intermediate

The transformation of the metal-oxo species to an N-oxo species has been proposed for the iron-oxo porphyrin system.[63,100] A potential energy surface, triplet spin state, was constructed for the distortion mode that converts the Ru-oxo complex to a species with increased N-O bonding. The N_{eq}-Ru-O angle, θ, was compressed from 90°, to allow comparison with the results of Veillard[100] and Jorgensen.[63] A soft potential energy surface resulted up to θ = 50°,

after which the total energy increases markedly. Up to θ = 50° there is no N-O bonding, as evidenced by a maximum atomic bond index of 0.06 and a minimum N-O distance of 1.67Å on the shallow portion of the potential energy surface. Stabilization of the HOMO (RuO π^*) of the Ru-oxo system, due to a decrease in the unfavorable overlap of the Ru dπ - O pπ antibonding combination, is counteracted by a destabilization of the Ru dπ - O pπ bonding combination (caused by a decrease in the favorable overlap). The doubly occupied bonding combination dominates the singly occupied antibonding combination with respect to their effects on the overall energetics. These considerations lead to a high energy barrier for N-oxide formation and reduce the possibility of the N-oxo mechanism for ruthenium. The results for cis-$[Ru(HN{=}CH{-}CH{=}NH)_2(NH_3)(O)]^{2+}$ (hereafter referred to as $Ru(IV)N_5O^{2+}$) are in agreement with the ab-initio analysis of Strich and Veillard[100] on Fe[porphyrin](O)(py) (py = axial pyridine) who found an N-oxo intermediate to be unfavorable, but opposite to the Extended HÜckel results of Jorgensen[63] on Fe[porphyrin](O)(H_2O).

Initial Formation of an Ion-Molecule Complex

At separations greater than $R_{C\text{-}Oxo} \approx 2.7$Å, energy minimization leads to the formation of a weakly bound (by ≈ 9 kcal mol^{-1}) ion ($RuN_5O^{2-\delta}$)-molecule ($C_2H_4^{+\delta}$) complex.

This ion-molecule complex is interesting in that it is similar to the charge-transfer complex which has been proposed by Bruice[31,101] in the epoxidation of olefins by oxo-chromium and oxo-iron porphyrins. One must be careful about extrapolating the results of "gas-phase" calculations to solution-phase experiments. The ground state for this complex is a triplet. Covalent C-Oxo bonding is virtually nonexistent (Atomic Bond Index ≈ 0.), and the Ru-Oxo/Olefin interaction is largely electrostatic.

Proceeding from the shallow ion-molecule minimum toward covalent C-Oxo distances incurs a small barrier, < 3 kcal mol^{-1}, at $R_{C-Oxo} \approx 2.5$Å. Geometry optimization after this barrier has been passed leads to local minima which are covalently bound. The minima are the bound epoxide; the oxometallocycle was never observed as a stationary point on the potential energy surface for the epoxidation of ethylene by the Ru-oxo complex.

[2+2] Cycloaddition Pathway

A [2+2] cycloaddition, to yield a four-membered M-O-C-C ring (referred to as an oxometallocycle), has been proposed by several workers.[46,102] Formation of an oxometallocycle by a [2+2] pathway is allowed due to the lowered C_s symmetry. Geometry optimization of structures in which the Ru-O and C-C bonds are parallel was carried out. The Ru-C bond was initially set to 2.3Å (slightly greater than the

Ru-C bond distance of 2.21Å in ruthenocene[96]). The resulting minimum showed almost no ethylene-metal oxo interaction: the C-C and Ru-O bonds do not change from their individually optimized bond lengths (R_{CC} = 1.32Å, R_{RuO} = 1.96Å); the H atoms maintain a planar arrangement around the ethylene C's; and the metal complex maintains an octahedral geometry. These calculations were repeated with the pentammine analogue, as it possesses more freedom in its bending modes and can distort out of the way to accommodate an oxometallocycle. Similar results to those presented above were obtained. These results suggest that the formation of an oxometallocycle intermediate in a concerted manner is not likely.

The unfavorable, planar [2+2] addition pathway results from repulsion between the occupied RuO π_y and C_2H_4 π MOs. The diabatic correlation diagram shows the correlation of the ethylene π with a high energy σ^* orbital in the products, Figure 2-2, that would result if an oxometallocycle was formed. This two-center, four-electron interaction is repulsive and leads to the unfavorable concerted [2+2] pathway observed, although the symmetry requirement is relaxed.

In RuN_5O^{2+} it is the RuO moiety which largely determines the reactivity. Removing the ligands from the RuN_5O^{2+} complex amounts to ignoring the small contribution

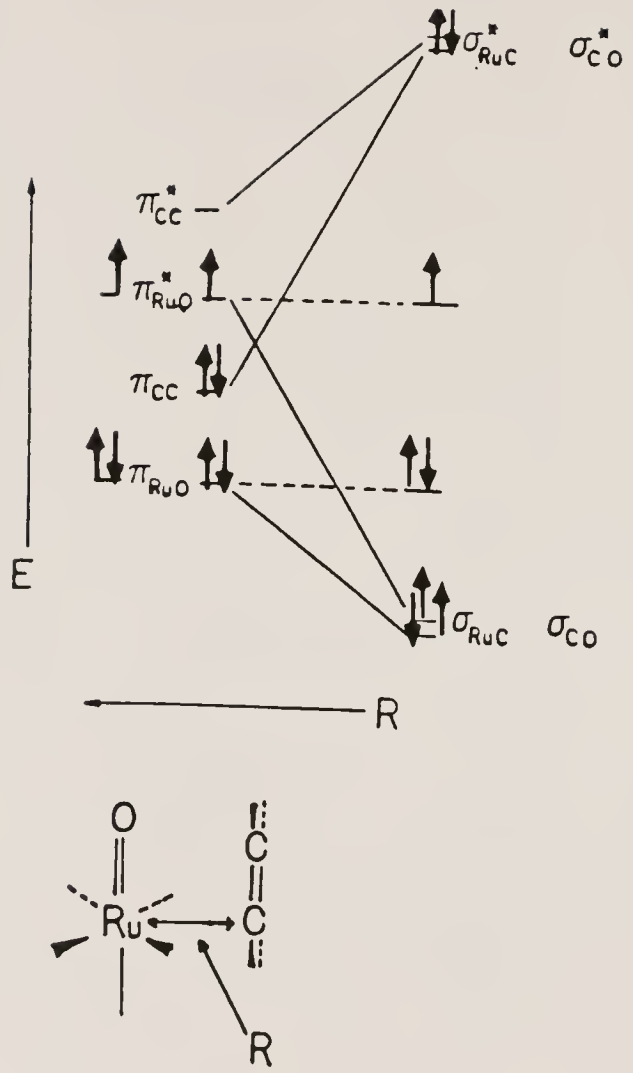


Figure 2-2: Schematic diabatic orbital correlation diagram showing the evolution of the active orbitals as a function of R for the concerted [2+2] pathway.

of the ligand orbitals to the frontier orbitals. These frontier orbitals are largely Ru 4d in nature. This approach is similar to that used by Sevin and Fontecave in their Extended HÜckel study of Fe-O catalyzed epoxidations.[92,93] The removal of five ligands results in the δ^* MO being lowered in energy. Thus, two electrons must be added to the Ru-oxo moiety in order to yield a species with the necessary $\pi^4\pi^{*2}$ electronic configuration. Ab-initio calculations performed on RuO and RuO^+ by ourselves and others[74] yield ground and low energy excited states with a $\pi^4\pi^{*2}$ electronic configuration over a range of Ru-O bond lengths. Our INDO/1 calculations describe these species quite well. An analysis of the INDO calculations for the concerted [2+2] pathway using RuO (R_{RuO} = 1.96Å) as the metal-oxo reagent reveals that the crossing of the bonding combination of the RuO π^* and the higher energy ethylene π^* with the antibonding combination of π_{CC} and RuO π occurs at R_{C-Oxo} and $R_{Ru-C} \approx$ 2.5Å, Figure 2-2, as evidenced by a transfer of electron density from the olefin to the metal-oxo fragment. These bond lengths are greater than typical C-O or Ru-C covalent bonds making the concerted [2+2] pathway unfavorable. The non-concerted pathway will be discussed in greater detail below. The geometries of the ethylene and Ru-oxo fragments were kept constant in this explorations of the Ru-oxo/olefin PES.

[1+2] Cycloaddition Pathway

Continuing along the concerted [1+2] pathway, after passing the small barrier from the ion-molecule minimum leads to a large repulsion between the occupied ethylene π MO and the oxo lone pair (largely p_z). As with the formation of cyclopropane by the least motion pathway from ethylene and methylene,[103] the concerted [1+2] addition of ethylene to the metal-oxo is disfavored, Figure 2-3. Once again using the Ru-O moiety and ethylene the orbital correlation diagram for the [1+2] pathway was constructed, Figure 2-3. A crossing between the antibonding combination of the oxo lone pair and the ethylene π MO with the bonding combination of the RuO π^* and ethylene π^* occurs at R_{C-Oxo} $\approx$ 2Å. This distance is, of course, greater than a covalent C-O bond, Figure 2-3.

Non-concerted [1+2] and [2+2] processes

Non-concerted [1+2] and [2+2] pathways were considered next, as the concerted pathways were shown to possess unfavorable two-orbital, four-electron repulsions. The concerted [1+2] and [2+2] pathways are connected by these non-concerted pathways. Structures on the non-concerted [1+2] and [2+2] pathways differ mainly by the Ru-O-C angle. Structures on the non-concerted [1+2] and [2+2] pathways possess Ru-O-C angles of $\approx$ 180° and $\approx$ 90°, respectively. The electronic energies of the open structures $[RuN_5OC_2H_4]^{2+}$

and [$RuOC_2H_4$] are calculated to be within 10 kcal mol^{-1} of each other depending on the exact geometry (Ru-O-C angle, orientation of the H's about the ethylene carbons, etc.). Based on the lower repulsions expected between any substituents on the olefin with the ligands of the complex for angles closer to 90°, i.e. the non-concerted [2+2] pathway, the non-concerted [1+2] trajectories would be expected to be more favorable for steric reasons. Also, all open structures optimized to epoxides regardless of Ru-C distance, even in those cases in which the Ru-C distance is less than the C-O distance. The Ru-C distance was changed by changing the Ru-O-C angle. Greater attention was focused on the non-concerted [1+2] pathways for these reasons. In the open structures the C-C bond distance is roughly between that of a single and double bond ($R_{CC} \approx 1.4$Å); the coordination about the terminal ethylene carbon is trigonal planar; the coordination about the non-terminal ethylene carbon is approximately tetrahedral; and the C-O bond length is close to a typical covalent value ($R_{CO} \approx 1.45$Å).[96]

Single-point INDO/1 calculations were performed for the concerted pathways, as well as the two geometric perturbations which characterize the non-concerted pathways. The RuO fragment ($R_{RuO} = 1.96$Å) was used to model the oxidant. Due to the importance of electron correlation in bond-making/bond-breaking processes an exact, quantitative description of the potential energy surface is difficult.

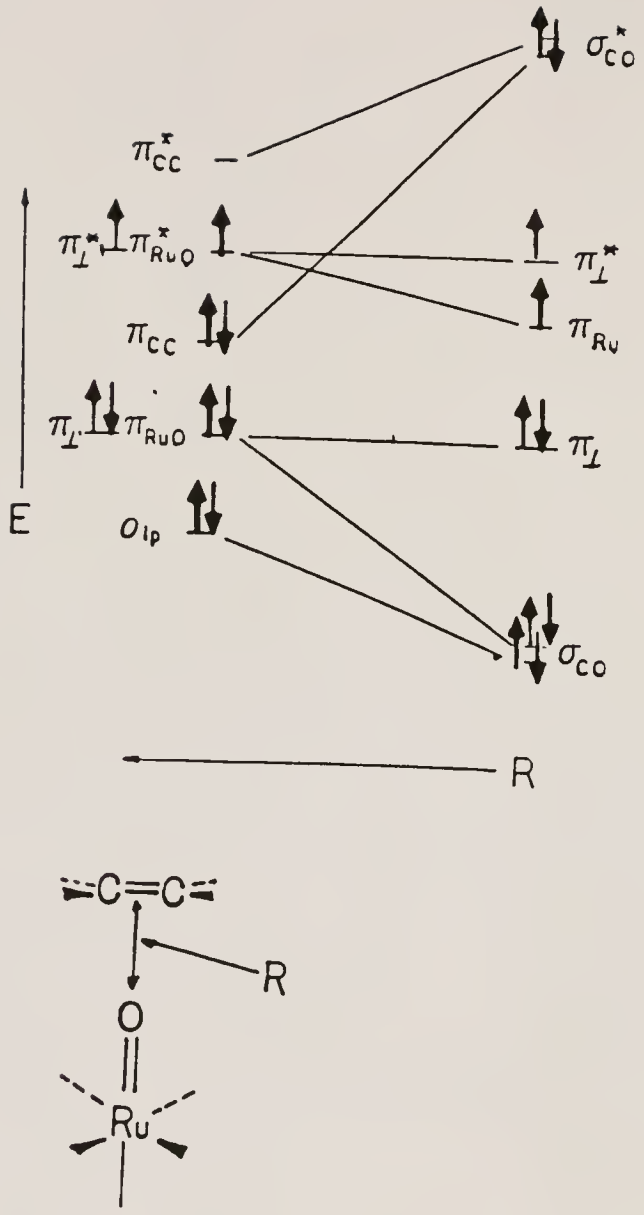


Figure 2-3: Schematic diabatic orbital correlation diagram showing the evolution of the active orbitals as a function of R for the concerted [1+2] pathway.

However, general trends are expected to be well described. The two geometric perturbations are shown in Figure 2-4. Φ, describes the motion of the ethylene off-center, and was varied from 0° to 90°, for R = 3.0Å, 2.5Å, 2.0Å, 1.5Å, and 1.0Å, Figure 2-4. Θ, which yields information about the process of canting, was also varied from 0° to 90° for the same distances, Figure 2-4. The PESs constructed (Φ x R x E and Θ x R x E) on the triplet manifold (all multiplicities gave similar results) are shown in Figures 2-5 and 2-6. As with the well known organic examples, a non-concerted trajectory results from a high barrier in the least motion, concerted pathway. Translation of the ethylene off-center (i.e. the center of the C-C bond is no longer co-linear with the Ru-oxo bond) from the non-concerted [1+2] trajectory decreases repulsion between the oxo lone pair and the ethylene π MO and allows for back bonding between the ethylene π^* and the O lone pair (these MOs have zero overlap otherwise). As evidence for decreased repulsion between the oxo lone pair and the ethylene π, the calculated splitting between the bonding and antibonding combinations of these two MOs decreases by 0.009 hartrees for a 10° perturbation off-center from the concerted [1+2] pathway at $R_{C-Oxo} \approx 2$Å. At relatively large separations on the concerted [1+2] pathway, R ≈ 2.5Å, perturbation of the ethylene off-center causes the total energy of the reactants to decrease.

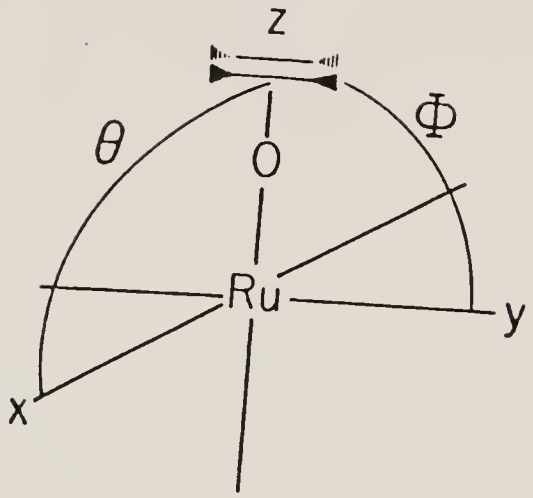


Figure 2-4: The two geometric perturbations which characterize the non-concerted pathways. The values in parenthesis are the Φ and θ values, respectively. Thus, (0°,0°) is the concerted [1+2] pathway and (90°,0°) is the concerted [2+2] pathway.

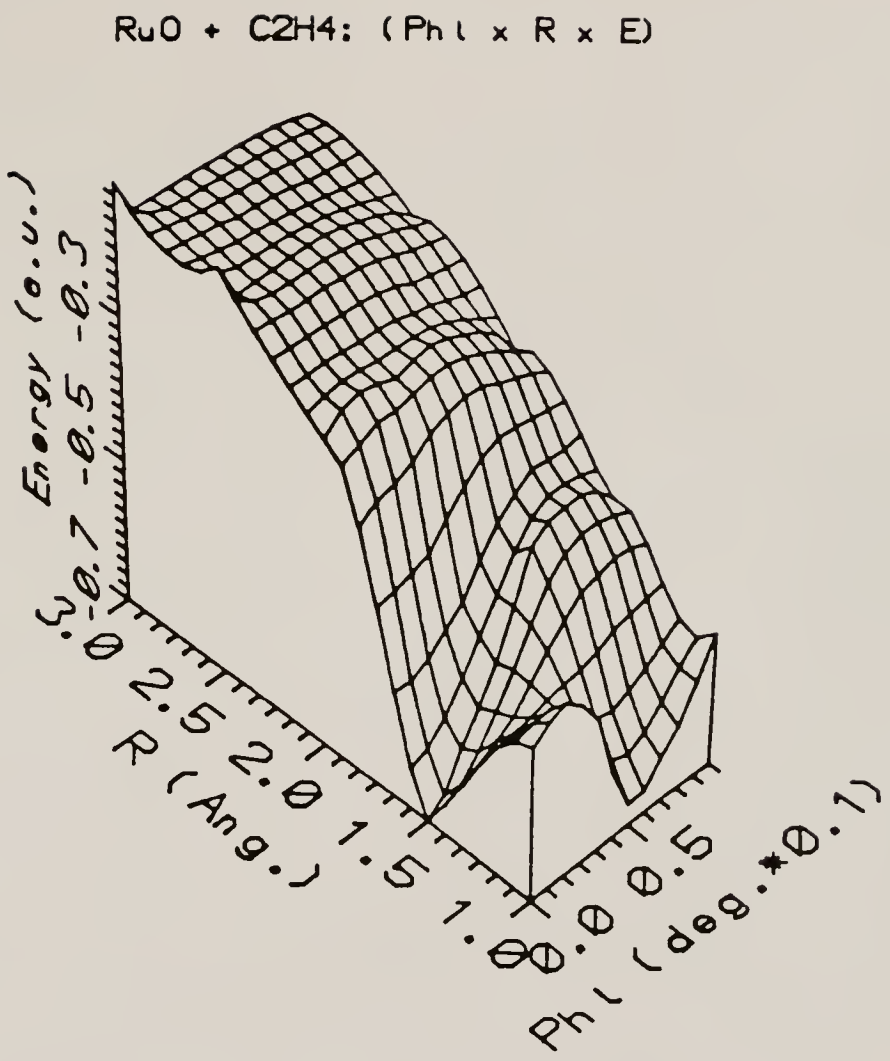


Figure 2-5: PES (Φ x R x E) for the coordinates discussed in the text and shown in Figure 2-4. This PES describes the perturbation of the ethylene fragment off-center of the vector which describes the Ru-O bond.

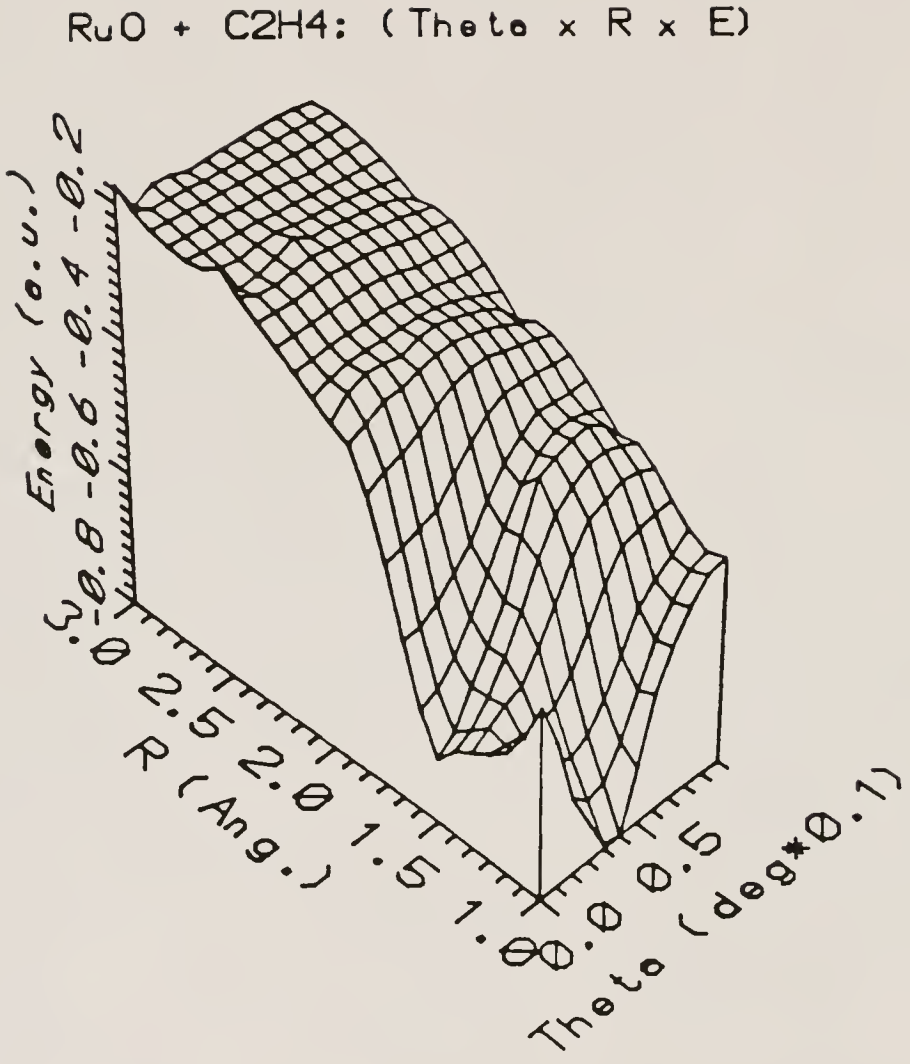


Figure 2-6: PES (θ x R x E) for the coordinates discussed in the text and in Figure 2-4. This PES describes the canting process of the ethylene fragment.

For example, at R = 2.5Å, Θ = 0°, moving from Φ = 0° to 10° decreases the total energy by 53 millihartrees (≈ 32 kcal mol^{-1}). As R approaches covalent values, R ≈ 1.5Å, perturbation off-center causes an increase in the total energy. This is consistent with the notion of stretching a covalent bond from its equilibrium bond length (C-O in this case). At R = 1.5Å on the concerted [1+2] pathway ($\Theta = \Phi$ = 0°), moving from Φ = 0° to 10° increases the total energy by 15 millihartrees (≈ 9 kcal mol^{-1}). Canting (i.e. rotation about the C-C axis such that the molecular plane of the ethylene is not perpendicular to the vector which describes the Ru-O bond) leads to a more stable pathway due to increased overlap of the ethylene π symmetry orbitals with the π symmetry orbitals of the Ru-oxo fragment. For non-canted pathways the π symmetry AOs of ethylene are orthogonal to at least one set of the RuO π orbitals. Canting removes this orthogonality, and allows interaction between the ethylene π symmetry AOs and both sets of RuO π orbitals. In the concerted [2+2] pathway the interaction of the π_{CC} with the π_{RuO} is not symmetrical due to the polarized nature of the latter MO (π(RuO-INDO) = 0.42 Ruπ + 0.91 Oπ compared to π(RuO-ab-initio) = 0.40 Ruπ + 0.92 Oπ). The π_{RuO} is concentrated to a greater extent on the more electronegative oxygen atom. Thus, C-O interaction is stronger than C-Ru interaction and provides the driving force for the observed non-concerted process. The decrease

in the repulsion between the O lone pair and the ethylene π provides the driving force for a non-concerted [1+2] pathway as it does for the analogous $CH_2 + C_2H_4$ --> cyclo-C_3H_6 reaction.[103]

Geometry optimizations of $RuN_5OC_2H_4^{2+}$ species reveal that a non-concerted process takes place once C-O bonding dissymmetry is induced, i.e. one C-O bond is nearly fully formed, while the second is virtually non-existent. In fact, starting with the ethylene on the concerted [1+2] pathway will lead to non-concerted pathways. As we saw for the shallow minimum at $R_{C-Oxo} \approx 2.7$Å (vide supra), there was already a slight dissymmetry in C-O bonding.

An on-center trajectory in which the vector that describes the Ru-O bond bisects the C-C bond and is perpendicular to the molecular plane of ethylene has approximately C_{2v} symmetry. Using the symmetry labels pertinent to the C_{2v} point group, these MOs transform under the following irreducible representations: C_2H_4 - π (a_1), π^* (b_1); RuO - π_x (b_2), π_y (b_1), π_x^* (b_2), π_y^* (b_1). Thus, the ethylene π^* may interact with the RuO π_y and π_y^* , but the ethylene π may not. Since the ethylene π and π^* MOs are of different symmetries they may not interact by a second-order process. Moving the ethylene off-center of the Ru-O bond reduces the symmetry to C_s and the pertinent MOs to the following irreducible representations: C_2H_4 - π (a), π^* (a); RuO - π_x (b), π_y (a), π_x^* (b), π_y^* (b). Interaction may now

occur between the a symmetry orbitals. In an on-center geometry the MO interaction diagram in Figure 2-7 applies. The ethylene π MO does not interact with the RuO π_y and π_y^* MOs for the reasons given above. Moving the ethylene off-center allows the doubly occupied ethylene π MO to interact with the MO (singly occupied) formed from the bonding combination of the RuO π_y^* and π_{CC}^* (Y^* in Figure 2-7). The doubly occupied bonding combination places more orbital density on the non-terminal ethylene carbon, i.e. C-O bonding is strengthened, Figure 2-8. An analysis of the PES for the RuO moiety and ethylene shows this effect. Even at the relatively far distance of R = 2.5Å (S(Cpπ, Opπ) = -0.01) the orbital described above changes from $Y^* + \pi_{CC}$ = 0.92 Olp (lp = lone pair) + 0.27 $C_n\pi$ + 0.27$C_t\pi$ ($\theta = \Phi = 0°$) to $Y^* + \pi_{CC}$ = 0.97 Olp + 0.18 $C_n\pi$ + 0.14$C_t\pi$ ($\theta = 0°$, $\Phi = 10°$). C_n is the non-terminal ethylene carbon; C_t is the terminal ethylene carbon. As R decreases to this effect becomes more pronounced. The singly occupied antibonding combination places more orbital density on the terminal ethylene C, i.e. the terminal C acquires radical-cation character, Figure 2-8. Translation of the ethylene from $\Theta = 0°$, $\Phi = 0°$ to $\Theta = 0°$, $\Phi = 10°$ at R = 2.0Å increases the spin density on the terminal (un-bound) carbon from -0.02 to +0.15 electrons. With a large amount of orbital density on the C_t in this frontier MO, interaction with the orthogonal RuO π_x^* can, upon further reaction, lead to oxometallocycle

or bound epoxide. As stated previously, the perturbation of the ethylene fragment to an off-center geometry increases mixing by the ethylene π MO. Chemically, the ethylene donates more electron density to RuN_5O^{2+} and becomes more electrophilic. The second-order mixing process places greater partial positive charge on the terminal carbon. This build up of positive charge on the terminal carbon makes attack at the electron-rich oxo, to yield epoxide, preferred in relation to attack on the high valent Ru, to yield oxometallocycle. These open structures are analogous to those species which were seen on the non-concerted [2+2] pathway (vide supra). The minima for the formation of a bound epoxide gave approximately octahedral L-M-L angles, R_{Ruo} = 2.1Å (compared to 2.07Å and 2.03Å for the compounds trans-$[RuCl_4(OH)(NO)]^{2-}$ and trans-$[Ru(NH_3)_4(OH)(NO)]^{2+}$ [96]), R_{CC} = 1.50Å(1.47Å in ethylene oxide[96]), R_{CO} = 1.43Å (1.44Å in ethylene oxide[96]).

Comparison of the [1+2] and [2+2] Intermediates

The preference for formation of a bound epoxide over an oxometallocycle intermediate can be analyzed by using basic frontier orbital concepts. The oxometallocycle arises as a result of the formation of σ_{CO} and σ_{MC} bonds and two O lone pairs. Formally, two electrons are transferred from the ethylene substrate to the Ru atom of the RuN_5O^{2+}.

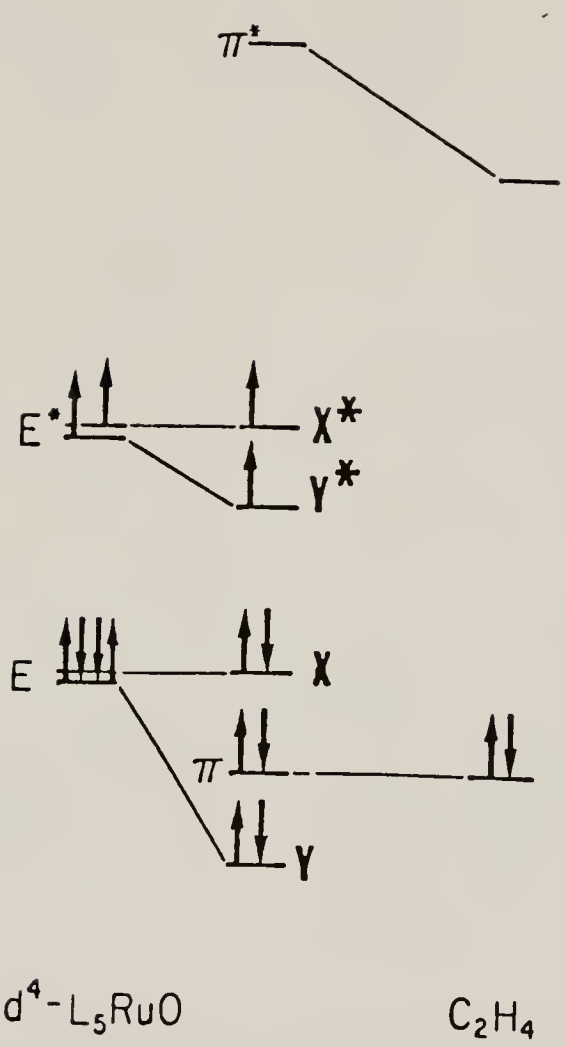


Figure 2-7: The MO interaction diagram between the π symmetry MOs for an on-center, C_{2v} geometry.

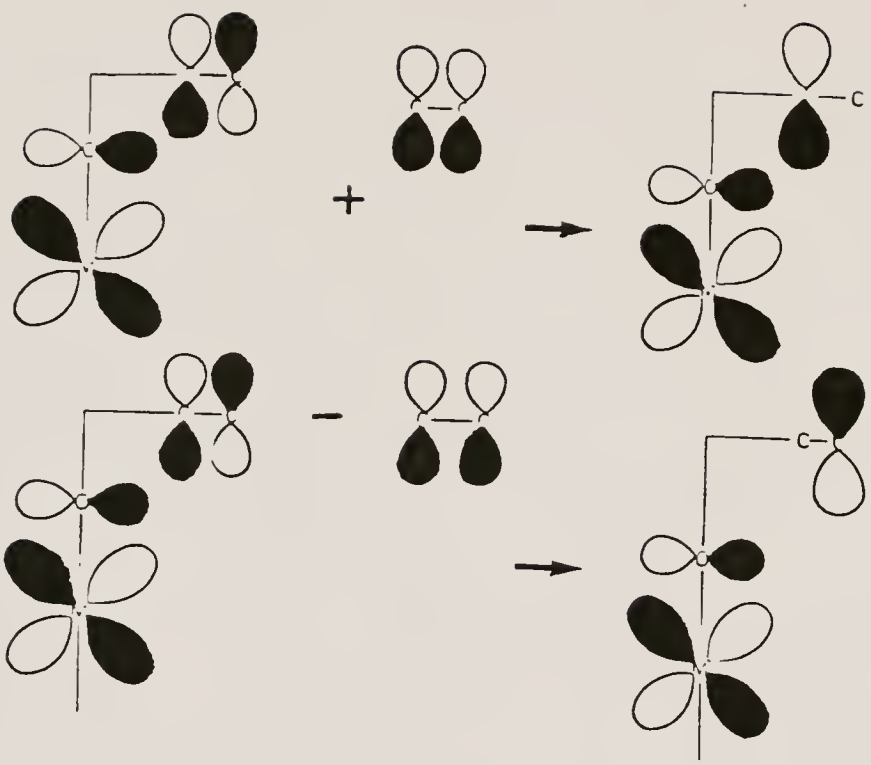


Figure 2-8: The mixing of the ethylene π MO that occurs as a result of the perturbation off-center from a concerted [1+2] pathway. The bonding combination reinforces C-O bonding. The antibonding combination (singly occupied) increases the orbital density on the terminal carbon.

With the INDO calculations showing the M-C bond to be approximately covalent and the M-O σ bond to be largely ionic, a d^5, Ru(III) complex results. The ground state of the oxometallocycle as derived from the INDO/1 calculation corresponds to the limiting case $[Ru(III)N_5(OC_2H_4^-)]^{2+}$ with a $|4d\delta^2\ 4d\pi^2\ (4d\sigma\text{-}C\sigma)(\alpha\beta\text{-}\beta\alpha)|$ electronic configuration. The oxometallocycle is a seven-coordinate structure.[104] Seven-coordinate geometries have been shown to possess a characteristic frontier orbital splitting of two non-bonding d orbitals below three antibonding d-orbitals making a d^5, seven-coordinate Ru(III) disfavored in relation to the bound epoxide which is a stable, low spin d^6, octahedral geometry. The INDO/1 calculation yields a $|d_{xy}^2\ d_{yz}^2\ d_{xz}^2\ d_{z2}^0\ d_{x2-y2}^0|$ electronic configuration for the bound epoxide. In fact, geometry optimization of an oxometallocycle with a starting structure in which the Ru-C and Ru-O bond lengths were 2.12Å and the C-O and C-C bond lengths were 1.50Å yields a bound epoxide minimum.

Conclusions

The theoretical results described here are in good accord with available experimental evidence. First, a charge-transfer complex, as has been proposed for epoxidations by ferryl and chromyl porphyrin systems,[31,101] is found as a minimum on the PES for $RuN_5O^{2+}\cdot C_2H_4$. Second, least motion [1+2] and [2+2] pathways are found to be

unfavorable, as for organic analogues, so that non-concerted processes are induced. The perturbation off-center causes a dissymmetry in the C-O bonding, leading to a non-concerted process. As the first C-O bond is formed, C-C π bonding is decreased, and the rotational barrier is lowered. For an open structure an 8.8 kcal/mole rotational barrier was calculated (3 kcal mol^{-1} for ethane, 65 kcal mol^{-1} for ethylene). In the epoxidation of cis-stilbene 5% isomerized product is found.[43] This suggests somewhat hindered rotation about the C-C bond; and that the rate of formation of the second C-O bond is competitive with C-C bond rotation. If this barrier were lower as in ethane more isomerized product (trans-stilbene oxide) would be expected in the epoxidation of cis-stilbene.

The slower rate for cis-stilbene (observed to be one order of magnitude less than that for the trans isomer) is consistent with a preference for canted pathways. Experimental and theoretical evidence[105] shows that trans-stilbene is planar while cis-stilbene is not. Thus, for the preferred canted approach modes the cis isomer is expected to have less favorable steric interactions.

In simple chemical terms, this reaction is a nucleophilic attack of the olefin directed at the oxo oxygen. For the reasons that we have already discussed in detail the oxygen atom transfer step proceeds in a non-concerted manner, i.e. one C-O bond forms and then the

second. Since this is a nucleophilic attack, a positive charge builds up on the terminal (non-bound) carbon of the substrate. Simple charge considerations lead one to predict, and INDO/1 calculations support, that $C^{\delta+}$-$O^{\delta-}$ interaction will be more favorable, and lead to bound epoxide, than $C^{\delta+}$-$Ru^{\delta+}$ interaction. The bound epoxide is a low spin, d^6 pseudo-octahedral complex and therefore, quite stable. The metal does not interact with the substrate directly but as an "electron sink" for the two electrons on being reduced from Ru(IV) to Ru(II). Exploring the interaction of the Ru-oxo complex with a substrate that possesses good donor ability, e.g. alcohols, will be interesting too see if the metal can play a direct role in oxidation.

CHAPTER 3
ALCOHOL OXIDATIONS

Introduction

Most of the proposed mechanisms for oxidations by P-450 models have concentrated on attack of the substrate on the oxo moiety, followed by oxidation, and subsequent removal of the oxidized product. Our previous INDO/1 investigation of epoxidation, using the model complex of this study, indicates that attack of the olefin directed at the oxo is the most favorable pathway and that bonding of the olefin to the metal does not occur. In this chapter we wish to investigate the oxidation of a substrate, i.e. alcohols, with good donor ability to see if the metal can play a direct role in oxidation or merely act as a reservoir for electrons. Six-coordinate Ru(IV)-oxo complexes have been shown by Meyer and co-workers[53,106] to be active alcohol oxidations catalysts. Two pathways are considered: activation of the alcohol C-H bond by the oxo and coordination of the alcohol to the metal.

Calculations

A molecular orbital analysis of different modes of interaction between cis-$[Ru(HN{=}CH{-}HC{=}NH)_2(NH_3)(O)]^{2+}$

(hereafter referred to as RuN_5O^{2+}) and methanol was performed using the INDO/1 method.[80,81] The calculation of both open- and closed-shell molecules was carried out using the Unrestricted Hartree Fock formalism[95] so as to allow for the direct comparison of energies. Geometry optimizations were of the gradient driven type.[97] Convergence of the gradient to stationary points on the potential energy surface was assumed when the maximum component of the gradient was less than 1.0×10^{-4} hartrees/bohr in all cases. This led to energies which minimized within 1.0×10^{-2} kcal mol^{-1}.

Results and Discussion

Electronic Structure of the Methanol Fragment

The electronic structure of the alcohol needs no in-depth discussion: the two lone pairs of valence orbital theory are combined in MO theory to yield two non-bonding MOs (NBMOs): a symmetric or σ non-bonding MO and an anti-symmetric or π NBMO. The σ and π labels for the NBMOs are with respect to the mirror plane of the alcohol (which contains the hydroxyl H, O and the alpha C). Thus, alcohol ligands may act as a π donor (albeit not to the extent of a chloride ligand) to the metal complex in a coordination mode in which C_α, O, H and Ru are co-planar.

C-H Activation at the Oxo Moiety

The relative energetics of C-H activation by the oxo of the Ru-oxo complex were compared to those of coordination of the alcohol to the ruthenium. Two limiting trajectories for the interaction of the C-H bond of MeOH to the oxygen of the Ru-oxo moiety were considered - a triangular pathway (i.e. the C-H bond of the methanol forms a triangle with the oxo and approaches in a perpendicular fashion), and a linear pathway (i.e. the Oxo-H-C angle is 180°).

A potential energy curve for both of the C-H activation pathways, i.e. linear and triangular, was constructed as follows. First, the geometries of the reactant fragments (i.e. MeOH and RuN_5O^{2+}) were kept constant. Second, single point INDO/1 calculations were used to evaluate the energy and other properties at various separations of the oxidant and substrate (as measured by the Oxo-H internuclear distance, R_{Oxo-H}) from R_{Oxo-H} = 3.2Å to R_{Oxo-H} = 0.94Å in approximately 0.1Å increments.

The triangular trajectory was calculated to be unfavorable at all internuclear distances with R_{C-Oxo} < 2Å. At points on the potential energy surface (PES) in which the C-Oxo distance is less than a typical covalent C-O bond (≈1.4Å[96]), but greater than an O-H covalent bond (≈0.96Å[96]), the potential energy surface is extremely repulsive.

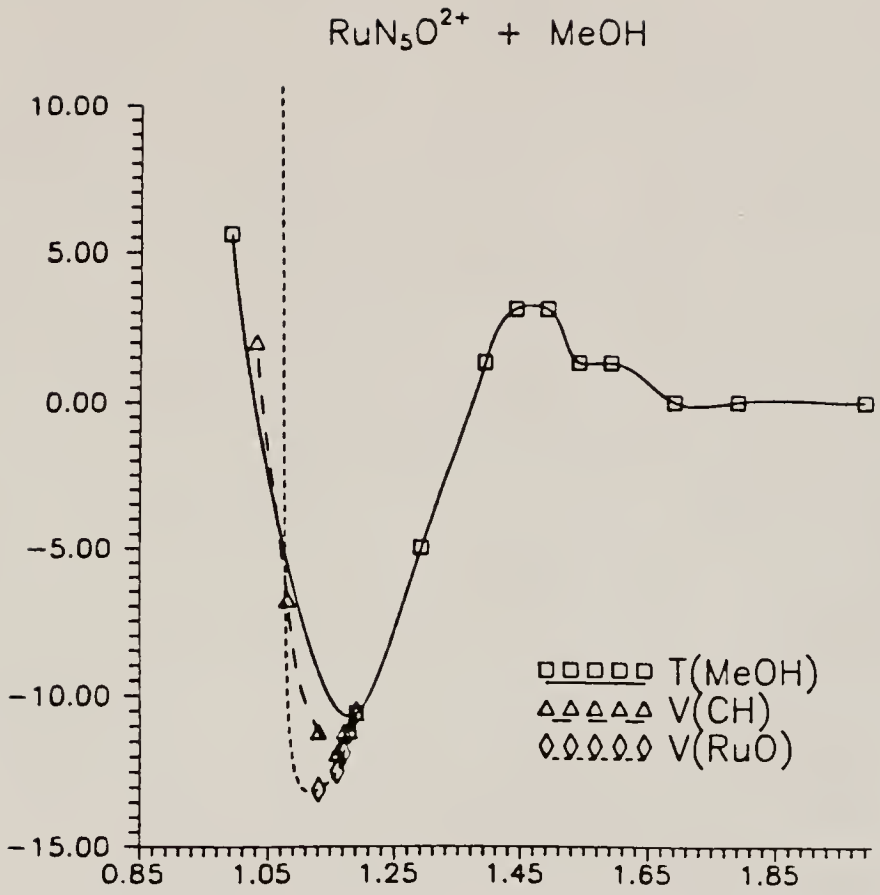


Figure 3-1: Potential Energy Curve for the translation of the entire methanol fragment relative to the Ru-oxo fragment in a linear orientation and with C-H and Ru-O stretching modes imposed upon the ion-molecule minimum.

The potential surface for the linear C-H-Oxo trajectory provides an energetically more favorable orbital interaction and less steric repulsions, Figure 3-1. The energy for $RuN_5O^{2+}\cdot MeOH$ at $R_{Oxo-H} \geq 1.7$Å is equal to the sum of the energies of isolated RuN_5O^{2+} and MeOH fragments. At $R_{Oxo-H} \approx 1.4$Å, the sum of the ionic radii of O^{2-} and H^+,[107] a slight barrier of 3.1 kcal mol^{-1} to further translation of the methanol, Figure 3-1, is found originating from a repulsive two-orbital, four-electron interaction between the Ru-O σ non-bonding MO (predominantly O $2p_z$) and the methanol C-H σ bond. Evidence for this is a polarization of the Ru-oxo active space such that electron density ($\approx$ 1 electron as determined by a Mulliken Population Analysis) is transferred from the O $2p_z$ to the largely unperturbed RuO π^* MOs. At $R_{Oxo-H} \approx 1.2$Å, Figure 3-1, there is a minimum which is calculated to be 10.6 kcal mol^{-1} below the separated fragments. Shortening of R_{Oxo-H} below 1.2Å causes a large increase in the total energy of the Ru-oxo/alcohol system, Figure 3-1.

The linear complex resembles a three-center, four-electron hydrogen bond. The atomic bond index between the oxo and the hydrogen at the minimum is 0.25 while that for the C-H bond is 0.65 (0.90 in "free" methanol) indicating a weak oxo-H bond. The $RuN_5O^{2+}\cdot MeOH$ interaction is significant, but it should be remembered that this is a calculation on a gas phase system and in solution this

interaction has to compete with the solvent shell around the complex (water or alcohol). Formation of this weakly bound species would be difficult in solution.

Assuming the linear ion-molecule complex can occur, two further geometric perturbations from the linear ion-molecule minimum, Figure 3-1, were explored with the intent of studying the energetics of closing the oxo-H bond to covalent distances, $R_{Oxo-H} \approx 0.96Å$.[96] First, a C-H stretching mode, V_{CH}, was calculated. The total energy decreases[108] for expansion of the C-H bond by about 0.04Å (and thus closing R_{Oxo-H} by a like amount), after which the total energy rises, Figure 3-1. Second, the Ru-O bond stretching mode, V_{RuO}, was explored. This yielded a decrease in the potential energy curve for $\delta R(Ru-Oxo) \approx +0.06Å$, after which the energy rises steeply, Figure 3-1. Thus, direct formation of a covalent oxo-H bond by either of these processes alone is not indicated. The third possibility is a concerted stretching along the C-H and Ru-O bond distortion modes. The difference in R_{Oxo-H} between the ion-molecule complex ($R_{Oxo-H} \approx 1.20Å$) and a covalent oxygen-hydrogen bond($R_{OH} \approx 0.96Å$[96]) is 0.24Å. Stretching the C-H and Ru-O bonds each by 0.12Å, in the ion-molecule complex, is calculated to increase the total energy by 52 kcal mol^{-1}. This energy is quadruple the experimental activation energy.[53,107]

Possible Seven Coordinate Intermediates

In their treatment of seven-coordinate complexes,[104] Hoffmann and co-workers noted a definite pattern of two low and three higher energy frontier orbitals (all largely metal d in character). This is significant, in the present case, as it confers relative stability (1st and 2nd order Jahn-Teller stability) to d^4 seven-coordinate transition metal complexes. The greater size of second-row transition metals lends further weight to the possibility of a seven-coordinate intermediate or transition state. Thus, a seven-coordinate Ru(IV) complex might be expected to be a relatively stable intermediate (or transition state). Experimentally,[53,107] there is a large, negative $\Delta S^{\ddagger}$ for the oxidation of MeOH by $[Ru(bpy)_2(py)(O)]^{2+}$ indicating that a strongly associated complex exists in the rate determining step. Also, seven-coordinate Ru(IV) complexes have been isolated and characterized by Pignolet and co-workers.[109] Based on these observations, an inner coordination-sphere expansion pathway could be proposed as a viable alternative or competing pathway to the C-H activation scheme.

Extended HÜckel calculations[104] on d^4 ML_7 (L = σ donor, π donor, or π acceptor) indicated that the pentagonal bipyramid (PBP7) is the preferred geometry over the capped octahedron (CO7) and the capped trigonal prism (CTP7) but only by a slight amount.

Seven-coordinate complexes can be obtained from an octahedral molecule by distortion to form the seven-coordinate precursor, followed by coordination of the seventh ligand. The term precursor, as used in the rest of this paper, refers to a structure in which the six-coordinate Ru-oxo complex has been distorted towards an arrangement which will allow for coordination of a seventh, i.e. ROH, ligand to produce the types of seven-coordinate complexes studied. Three seven-coordinate structures were investigated - the pentagonal bipyramid (PBP7), the capped octahedron (CO7), and the capped trigonal prism (CTP7). The CTP7 possesses a higher calculated activation energy (15.6 kcal mol^{-1}) than does the PBP7. The CO7 was discounted due to significant steric hinderance.

The PBP7 is formed by the expansion of the equatorial plane to accommodate one extra ligand (i.e. 90° L-M-L angles are compressed to 72°). Geometry optimization of the six-coordinate Ru-oxo complex, on the triplet manifold, was performed. A minimum with a Ru-oxo bond length of 1.96Å, an average Ru-N bond length of 2.06Å, and a pseudo-octahedral metal environment was obtained. These results agree very well with the experimental determinations of Che[98] which yield Ru-O and Ru-N bond lengths of 1.77Å to 1.86Å and 2.07Å to 2.16Å, respectively, for Ru(IV)-oxo complexes with nitrogen ligands. The perturbation of the equatorial N-Ru-N angles to a structure with 72° L-M-L angles (PBP7 precursor)

was calculated to cost 9.6 kcal mol^{-1}. The ground state remains a triplet.

Due to the lower calculated activation energy for the formation of the pentagonal bipyramidal complex, along with the structural and electronic similarity of seven-coordinate complexes (as evidenced by their fluxionality[110]), only the coordination of MeOH to the PBP7 precursor was investigated. The calculations indicate no activation barrier for coordination. The total energy decreases as R_{MO} decreases, up to a metal-oxygen (from ROH) distance of 2.3 - 2.4Å. Covalently bound seven-coordinate species are formed; the calculated binding energies are 30.0 kcal mol^{-1} (triplet) and 30.3 kcal mol^{-1} (singlet). R_e(Ru-O) is 2.40Å for the triplet $RuN_5O(ROH)^{2+}$ and 2.35Å for the singlet analogue; the singlet state is 18.2 kcal mol^{-1} below the triplet state at R(Ru-o) = 2.35Å for $RuN_5O(ROH)^{2+}$.

If we take the calculated minimum of the metal-coordination route and rotate the methanol ligand about an axis perpendicular to H-O-C_α plane and passing through the oxygen, Figure 3-2, a further 38 kcal mol^{-1} of stabilization is calculated. Although this amount seems spurious it does point to a stabilization from increasing C-H···Oxo interaction. Thus, we are left with a cyclic association complex and one which seems to combine the attributes of both proposals, Figure 3-2.

Further Reaction of a Seven-Coordinate Complex

While the main goal of this research was to compare initial substrate/oxidant interaction, it is interesting to probe the nature of any subsequent reaction of the Ru(IV)-oxo/alcohol complex to produce the Ru(II)-OH_2 and carbonyl products. The mechanism which Meyer and co-workers have proposed after an exhaustive mechanistic study[53,106] is given in Equations 1 - 3.

$$N_5Ru\text{-}O^{2+} + HC(OH)R_2 \overset{\leftarrow}{\rightarrow} N_5Ru\text{-}O^{2+},HC(OH)R_2 \quad (1)$$

$$N_5Ru\text{-}O^{2+},HC(OH)R_2 \rightarrow [N_5Ru\text{-}O\cdots H\text{-}C(OH)R_2]^{2+} \rightarrow N_5Ru\text{-}OH^{+},C(OH)R_2^{+} \quad (2)$$

$$N_5Ru\text{-}OH^{+},C(OH)R_2^{+} \rightarrow N_5Ru(OH_2)^{2+} + O{=}CR_2 \quad (3)$$

This mechanism entails association, Eqn. 1, "hydride transfer", Eqn. 2, followed by a proton transfer, Eqn. 3. The most favorable conformation for a donor with one σ and one filled π orbital (a single-faced donor[104]) in a PBP7 is with the π orbital of the ligand in the equatorial plane of the complex. Maximum overlap of the ROH σ NBMO with the virtual $d\delta$ (the vacant hybrid orbital which points in the direction of the missing seventh ligand) is provided. Destabilizing two-center, four-electron repulsions are minimized by keeping the π functions orthogonal. In this conformation the alkyl or hydroxyl hydrogens of the alcohol are ideally positioned to transfer to the oxo oxygen. One of the orbitals that the alcohol is using to transfer

electron density to the metal is almost a pure p orbital ($C_i \approx 0.92$ in an INDO/1 calculation) and the other is approximately 67% p-character ($\approx sp^2$ hybridization), p orbital density is transferred to the metal, leaving proportionately more s electron density on the oxygen. In accord with Bent's Rule[111] and in comparison to simple hydrocarbons as the percentage of s character increases the angles involved, the C_α-O-H angle of the alcohol in the present case, increase. This has the effect of moving the hydrogens (alkyl and hydroxyl) closer to the Ru-O moiety of the RuN_5O^{2+} complex. At this point two things can occur: the two hydrogens (i.e. those which convert the alcohol to the carbonyl) transfer in two separate and discrete steps or these two hydrogen atoms can transfer at the same time in one concerted process. Assuming the two-step process takes place, a complex with the formula $[RuN_5(HOCH_2)(OH)]^{2+}$ will be formed. The nature of this reactive moiety is subject to much speculation,[53,106] as is the nature of the H species which is transferred - two limiting configurations would seem to be reasonable, $[Ru(IV)N_5(HOCH_2^-)(OH^-)]^{2+}$ and $[Ru(III)N_5(HOCH_2^{\cdot})(OH^-)]^{2+}$. For a seven-coordinate pathway to be favorable the former configuration would have to make a significant contribution to the ground state wavefunction. The second H transfers to form a $Ru(II)OH_2$-carbonyl species.

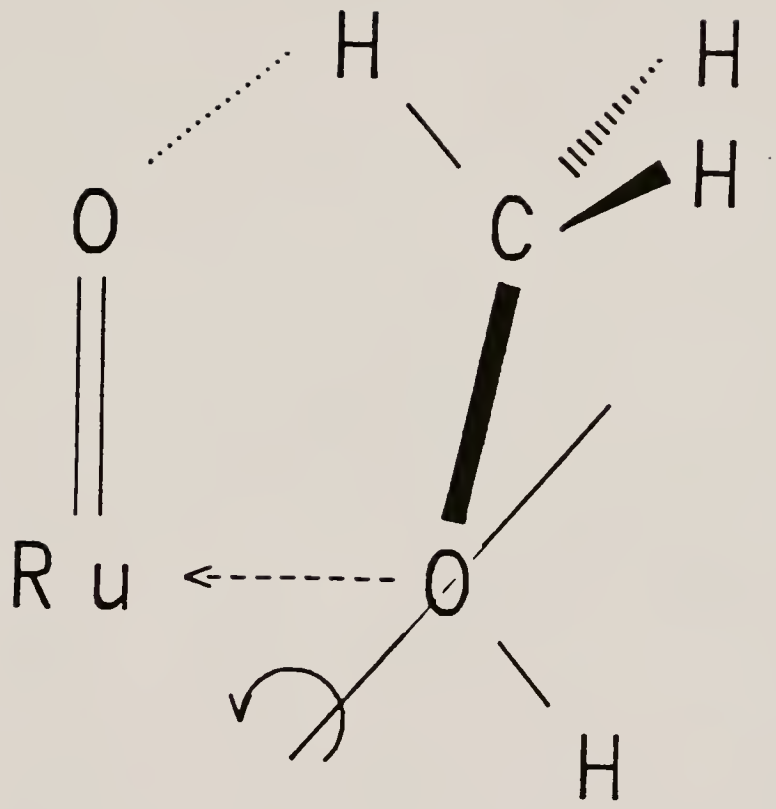


Figure 3-2: Structure of "cyclic" intermediate which combines C-H-Oxo and M-O pathways.

This transfer of the second hydrogen can be envisioned as occurring by two different processes: the second hydrogen transfers directly to the Ru-OH or it may be abstracted by a solvent molecule which then reacts with Ru-OH to yield Ru-OH_2. After the second hydrogen transfer two things happen:

1) The strong alkoxide/alkoxy radical ligand is replaced by a weaker O bound carbonyl ligand.

2) The very strong oxide (O^{2-}) ligand is replaced with the weaker OH_2.

Thus, the electron density on the metal increases (also by donation from the alcohol). Since seven-coordinate complexes are averse to d orbital counts greater than 4, the carbonyl jettisons and the six-coordinate $RuN_5(OH_2)^{2+}$ is obtained.

Our present results deal most directly with the nature of the association complex in Equation 1. What light can we shed upon the subject? We proceed by looking at the arguments against a seven-coordinate intermediate. They are: no precedent for coordination sphere expansion, rate of ^{18}O exchange (between RuO and $^{18}OH_2$) is slow, and no spectrophotometric evidence exists for such an intermediate.[53,106]

As we have seen there <u>are</u> precedents which allow us to propose a seven-coordinate association complex. First, simple frontier MO considerations point to stability for d^4 seven-coordinate complexes[104] Second, d^4 complexes of the

iron triad have been characterized by Pignolet[109] and an $[Os(IV)(bpy)(PPh_3)_2H_2(CO)]^{2+}$ by Meyer[112] (note that the ionic radius of the hydride is quite large, 208pm[113]).

We would expect water to form association complexes since it is a comparable ligand to alcohols and is sterically less demanding. However, once this association complex is formed the water is at a disadvantage with respect to scrambling of the ^{18}O label for various reasons. First, the homolytic bond strength of the O-H bond (119 kcal mol^{-1}) in water is significantly larger than the O-H bond in alcohols ($\approx$ 103 kcal mol^{-1}) and the C-H bond in alcohols ($\approx$ 92 kcal mol^{-1}). Experimental[114,115] and theoretical[74] analyses of Ru-O systems have pointed to the similarity of the RuO moiety to O_2 and the radical nature of RuO complexes. Thus, we would expect the "hydride transfer" to entail hydrogen atom abstraction followed by intramolecular electron transfer. Given the much greater strength of the O-H bond in water, H atom abstraction would be difficult. The second barrier to H atom transfer from water arises from the fact that the H atoms of water would be pointing away from the RuO π MOs (the orbitals where unpaired electron density resides to the greatest extent). If this scrambling arises from proton transfer the dihydroxy species formed will contain two symmetry inequivalent hydroxyl groups. This may be the cause of the observed lack of ^{18}O scrambling. The lack of spectrophotometric evidence for a

seven-coordinate association complex may be due to there only being a very small, but kinetically important, concentration of this complex.

There are other benefits of the combined C-H···Oxo/M-O interaction pathway. In the linear C-H···Oxo pathway a repulsive two-orbital, four-electron interaction between the MOs which corresponds to the C-H σ bond and the Oxo lone pair must necessarily arise. Bringing the C-H bond from the side allows for greater interaction between the C-H bond to be activated and the RuO π system - the orbitals which essentially define the reactivity of these and most metal-oxo complexes.[13] In a linear C-H···Oxo pathway the C-H bond to be activated is orthogonal to RuO π MOs making direct interaction impossible. In this "cyclic" intermediate the coupling of electron transfer and RuN_5O^{2+} vibrational modes that Meyer has proposed[53,106] may occur. Incidentally, Groves[116] has proposed for C-H activation of alkanes by ferryl porphyrin systems just such an approach (i.e. the C-H bond approaches the metal-oxo moiety from the side and directed at the oxo). Also, coordination of the alcohol to the metal provides for activation of the alcohol by transfer of electron density from the alcohol to the high-valent Ru atom. Our INDO/1 results indicate a significant acidification of the hydroxyl proton upon coordination to the metal. Thus, proton abstraction is facilitated by pre-coordination to the metal.

Summary

The INDO/1 results indicate that for the oxidation of alcohols by a six-coordinate Ru(IV)-oxo complex, alcohol coordination is comparable with, if not more favorable than, a C-H activation mechanism. The linear interaction of a C-H bond in methanol with the oxo oxygen leads to a loosely bound ion-molecule interaction with a oxo-H distance of 1.2Å. The formation of a covalent oxo-H bond, corresponding to hydrogen transfer, is costly in terms of the total energy of the system for various modes. The pentagonal bipyramid is calculated to present the best combination of favorable electronic and steric interactions. The calculated barrier for the formation of the PBP7 complex is 9.6 kcal mol^{-1}. Further interaction after the seven-coordinate association complex is formed increases C-H···Oxo interaction. Thus, the preferred pathway combines both proposals, i.e. pre-coordination of the alcohol and C-H···O interaction.

This study of alcohol oxidations by a six-coordinate, high-valent metal-oxo complex with nitrogen ligands (i.e. a P-450 model) shows that when the substrate has a good donor ability direct metal participation in the oxidation pathway is plausible. Most proposed mechanisms for oxidation by P-450 models involve the metal only indirectly as a receptor for two electrons. Our results suggest that metal participation may be important; in the oxidation of

substrates that possess good donor ability, i.e. alcohols, amines, and perhaps sulfides, the substrate may ligate to the metal in the course of the oxidation. Unfortunately, the Ru-oxo complex which we have studied has not been reported to be active for amine dealkylations or the hydroxylation of alkyl amines. This six-coordinate Ru-oxo complex has been shown to oxidize sulfides[54] which are, therefore, good subjects for further theoretical scrutiny.

CHAPTER 4
SULFIDE OXIDATIONS

Introduction

In the present research attention has been concentrated on the oxidation of sulfur to sulfoxides and sulfones. The main purpose of this chapter is to continue our investigations into the oxidation of organic substrates using the same model cis-$[Ru(HN=CH-HC=NH)_2(NH_3)(O)]^{2+}$ catalyst. Interaction of the sulfur with the oxygen and metal atoms of the Ru-oxo active site is considered. The organic sulfides are good donors and acceptors and should provide an interesting case for comparison with the other substrates (olefins and alcohols). Furthermore, the same moiety of the substrate (the S atom) is interacting with either end of the metal-oxo oxidant. The effect of the 3d orbitals on the bonding interactions of the sulfur are of interest and discussed where pertinent.

Calculations

The majority of calculations performed in the present work were of the semi-empirical INDO/1[80,81] variety, unless otherwise noted. All INDO/1 calculations were run two times: with and without 3d orbitals on the sulfur atoms. It

was found in the INDO/1 calculations that excluding 3d orbitals had the same effect as employing a severely contracted ($exponent_{3d}$ = 100.) Slater-type function for the radial portion of the atomic orbital. An exponent of 1.731 for the S 3d orbitals was chosen in those INDO/1 calculations in which the sulfur atom had a 3d basis. Ab-initio calculations were run using the HONDO-5 program.[117] Ab-initio and semi-empirical geometry optimizations were of the gradient-driven type and included electron correlation (Moller-Plesset perturbation theory to second-order[118]) for the ab-initio optimizations.

Results and Discussion

Electronic Structure of the Ru-oxo model.

The electronic structure of the six-coordinate Ru(IV)-oxo complex has been discussed in detail elsewhere and need not be repeated here.

Electronic Structure of the Sulfide Fragment

The proper modeling of the subtle effects of adding electronegative oxygen atoms to sulfur and excluding/including 3d orbitals is crucial for this study. To ascertain the suitability of the INDO/1 method for this research, geometry optimizations of SH_2, SOH_2, SO_2H_2 where carried out and compared with experiment, where available,

or with ab-initio calculations. The results of the INDO/1 calculations are summarized in Table 4-1, and are, in general, quite good. The electronic structure of C_{2v}, hydrogen sulfide needs no in-depth discussion.[119]

The effect of the 3d orbitals is always of interest when discussing the electronic structure of the second-row main group elements. The 3d orbitals may mix, in a second-order way (hybridization in valence bond terminology), into the correct symmetry sp-basis molecular orbitals of hydrogen sulfide. The 3d orbitals transform as $2a_1$ (z^2,x^2-y^2) + a_2 (xy) + b_1 (xz) + b_2 (yz) under the C_{2v} point group. Since the 3d orbitals are higher in energy than the 3s and 3p AOs, their effect will be to mix into the MOs which contain these AOs in a bonding manner,[120] and lower their energies. An INDO/1 calculation indicates this orbital energy lowering to be minimal, with values ranging from 2 to 25 millihartrees (1 millihartree $\approx$ 0.6 kcal/mole). An INDO/1 geometry optimization of hydrogen sulfide was run with and without the 3d orbitals. The theoretical results are summarized in Table 4-1. The inclusion of the 3d orbitals gives a lower energy (expected on the basis of the variational principle), as well as shorter bond lengths and smaller bond angles, indicating that the 3d orbitals are strengthening the S-H bonds. The bond lengths and angles are closer to experimental values for the basis which includes 3d AOs.

Table 4-1
Effect of 3d AOs on the Geometry of Sulfur Species

Species	Method	3d exponent	R_{SH}[a]	R_{SO}	θ(HSH)	θ(OSO)
H_2S	INDO/1	1.731	1.37	--	93.39	--
H_2S	INDO/1	100.0[b]	1.36	--	96.12	--
H_2S	expt.	--	1.33	--	92.2	--
H_2SO	INDO/1	1.731	1.37	1.52	90.7	--
H_2SO	INDO/1	100.0	1.37	1.73	95.8	--
H_2SO	ab-initio[c]	?[d]	1.34[e]	1.47	100.	--
H_2SO_2	INDO/1	1.731	1.37	1.52	104.1	118.3
H_2SO_2	INDO/1	100.0	1.38	1.74	103.3	127.0
H_2SO_2	ab-initio[f]	?	1.35	1.44	?	121.6

a Bond lengths (Å); bond angles (°); energies (a.u.).

b The value of 100.0 was used for the S 3d AO exponent to replace the default value of 1.731.

c See Reference 121.

d A question mark indicates that the specified quantity was not reported by the authors.

e A value of 1.34Å for the S-H interatomic distance was assumed and kept constant.

f See Reference 122.

Electron withdrawing groups on the sulfur will increase d orbital participation by d orbital contraction and energy lowering of these orbitals. Thus, H_2SO and H_2SO_2 will have a larger 3d orbital "effect." This is seen in the calculations which give a total 3d orbital population of 0.028, 0.403 and 0.767 electrons for isolated SH_2, SOH_2 and H_2SO_2, respectively. The INDO/1 method gives reasonable values as compared to the ab-initio results in terms of geometry optimizations. For SOH_2 and SO_2H_2, the effect of the 3d AOs on the S-H bond lengths is minimal while S-O is much reduced. The S-O bond changes from an approximately single bond value (the average of X-X in HXXH, X = S and O, is 1.77Å) to double bond value (the S-O bond length in SO_2 is 1.43Å).[96] The calculated Atomic Bond Indices are consistent with this interpretation, changing from 1.87 to 0.65 upon the severe contraction of the 3d orbitals. The effect of 3d orbital participation in analogous compounds is the subject of two excellent papers by Hoffmann and co-workers[123] and by Van Wazer and Absar.[124]

Direct Sulfur-Oxygen Interaction: Linear Coordination Mode

The interaction of the sulfur atom of the hydrogen sulfide molecule with the oxo oxygen of cis-$[Ru(HN{=}CH{-}HC{=}NH)_2(NH_3)(O)]^{2+}$ was investigated in two distinct modes: linear, with the Ru, O, S and H atoms (from SH_2) co-planar with the Ru-oxo bond and bent with respect to this plane.

This affords two different modes of interaction. In the linear interaction mode there is both a σ and π interaction with the two lone pair combinations. In the bent interaction mode there is only a σ interaction with one pair while the other remains essentially non-bonding.

The linear interaction between the sulfur and oxo decreases the total energy of the Ru-oxo/sulfide system until a covalently bound minimum is reached, regardless of the sulfur basis (sp or spd) or multiplicity, Figure 4-1. At 2.07Å, spd basis and triplet spin state, there is a slight polarization of the Ru-oxo fragment which entails the transfer of 0.25 electrons from the RuO σ to π manifold. This transfer of electron density from the σ to π is reminiscent of the polarization of RuO by the C-H bond of methanol in the C-H activation mode of alcohol oxidations. However, unlike that case there is no activation barrier present. This is a result of the polarization of the Ru-oxo MOs being much less in the sulfide case than in the alcohol case (0.25 vs. 1.0 electron). A Mulliken Population Analysis[125] indicates that the electron density comes from the O $2p_z$ (the major component of the oxo lone pair). The S-H atomic bond index changes little (0.95 to 0.93) indicating that the orbital responsible for this polarization is the non-bonding, molecular orbital. The sum of the 3d orbital populations remains at 0.02 electrons. However, the removal of the sulfur 3d orbitals increases the

polarization of the RuO caused by the hydrogen sulfide significantly. The dipole moment decreases upon inclusion of the 3d orbitals from 3.58 to 1.98 Debyes. Thus, the effect of the 3d orbitals is mainly electrostatic.

The minima for linear substrate/oxidant interaction occur at $R_{SO} \approx 1.48$ to 1.88Å depending on the multiplicity and S basis, Figure 4-1. The sulfur 3d AOs are important in the formation of covalently bound S-O species. The S-O bond distances in SO_2 and SO_3, which have some double bond character, are 1.43Å and 1.43Å, respectively.[96] The increase in energy on the PE curve is caused by too large a polarization of the O lone pair by σ pseudo-symmetry orbitals on sulfur. For example, on the triplet curve, sp sulfur basis, the translation of the sulfide from the minimum energy structure is accompanied by a large increase in transfer of electron density from the RuO σ to π manifold and a jump in the positive charge of the sulfide (+0.261 at the minimum to +0.629 at $R_{SO} \approx 1.58$Å). The 3d orbitals act to lower the dipole moment of the sulfide and thus this excessive polarization of the RuO moiety occurs at a smaller S-O interatomic distance. In both cases there is a shift from a triplet to singlet ground state which allows the S-O bond length to shorten further. This is a result of two electrons being transferred from the sulfide to the Ru-oxo fragment to produce a d^6 pseudo-octahedral complex.

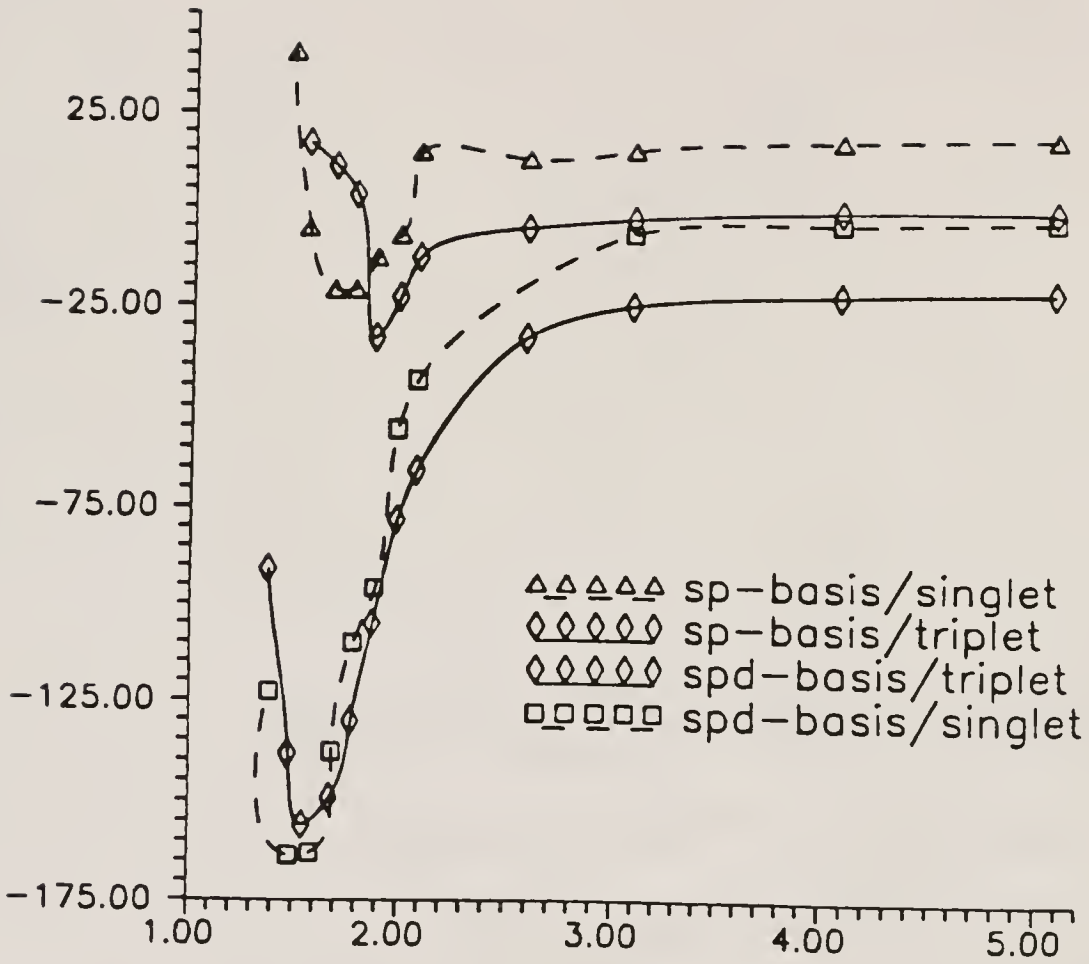


Figure 4-1: PE curves for interaction of Ru-O + SH_2 (spd or sp S basis and singlet or triplet multiplicity) in the linear mode.

In all cases of interaction directed at the oxo the bonding between the sulfur and the ruthenium is minimal with atomic bond indices close to zero.

In summary, a linear interaction between the sulfide substrate and the Ru-oxo catalyst is favorable up to covalent S-O distances. The 3d orbitals play an important, if indirect, role. They serve to lower the dipole moment of the sulfide by making the S-H bonds more covalent or equivalently by reducing the amount of charge separation in these bonds. This lowering of the dipole moment helps what is largely an electrostatic interaction be energetically feasible by lowering the amount of electronic reorganization which must occur within the Ru-oxo fragment before covalent S-O bond formation. The π symmetry non-bonding MO has a minimal effect on the bonding.

Direct Sulfur-Oxygen Interaction: Bent Coordination Mode

The geometric perturbation of the hydrogen sulfide fragment from a linear to a bent coordination mode serves to alter one major factor. The two lone pairs of H_2S can be combined to yield σ and π NBMOs. In the linear interaction mode R_2S is a σ and π donor to the Ru-oxo moiety. Distortion to the bent mode diminishes π donor ability. Thus, the distortion from a linear to bent orientation reveals the effect of the π-donor ability of the substrate on its interaction with cis-$[Ru(NH{=}CH{-}CH{=}NH)_2(NH_3)(O)]^{2+}$.

The formation of the bent structure is of particular interest since this allows the local OSH_2 moiety to attain the geometry of an O-bound sulfoxide, i.e. approximately tetrahedral geometry about the sulfur.

The results for this geometric distortion with various spin multiplicities and sulfur basis sets are given in Tables 4-2 to 4-5. A comparison of the potential energy surfaces, Tables 4-2 to 4-5 for the singlet and triplet spin states shows that the effect of the 3d AOs is similar to that for the linear orientation. The 3d orbitals allow the favorable region of the potential energy surface to be extended to covalent S-O distances. This is due, once again, to a diminution of the sulfide dipole moment by mixing of the S 3d AOs into the S-H bonding orbitals in a bonding way. A comparison of the potential surfaces with a sulfur spd basis indicates that as the interaction becomes more covalent the singlet and triplet manifolds approach each other. This is due to a transfer of electron density from the sulfide fragment into the Ru-oxo fragment (vide supra).

There is for all spin states and sulfur bases considered, a stabilization upon the conversion from a linear to bent sulfide orientation. The origin of this phenomenon is the stabilization of the S-O π^* upon bending.

Table 4-2
Conversion from Linear To Bent SH_2(spd) Orientation(3)[a]

	R(S-O)Å	1.08	1.58	2.07	2.57	3.07
Φ[b]	180°	1.629[c]	0.056	0.068	0.083	0.087
	175°	1.630	0.055	0.068	0.083	0.087
	160°	1.615	0.056	0.069	0.107	0.087
	144.75°	1.599	0.035	0.062	0.085	0.090
	130°	1.583	0.014	0.058	0.087	0.091
	115°	1.580	0.002	0.054	0.090	0.092
	109.5°	1.583	"0"[d]	0.054	0.092	0.093

a The first number in parenthesis of the title for Table 4-2 through Table 4-5 refers to the basis set, principal quantum number = 3, used for the sulfur atom; the second number in parenthesis refers to the overall spin multiplicity of the interacting Ru-oxo/SH_2 systems.

b Φ is the angle between the SH_2 molecular plane and the vector which describes the Ru-O bond.

c The energies are given in hartrees relative to the calculated minimum.

d "0" = -131.234 hartrees; other energies are relative to the "0" value and are in hartrees.

Table 4-3
Conversion from Linear To Bent SH_2(sp) Orientation(3)

	R(S-O)Å	1.08	1.58	2.07	2.57	3.07
Φ[a]	180°	1.635[a]	0.071	0.011	0.023	0.027
	175°	1.638	0.071	0.011	0.023	0.027
	160°	1.596	0.062	0.009	0.026	0.028
	144.75°	1.672	0.045	0.005	0.025	0.029
	130°	1.590	0.028	0.003	0.027	0.030
	115°	1.587	0.017	0.001	0.030	0.032
	109.5°	1.590	0.015	"0"[b]	0.031	0.033

a See footnotes in Table 4-2.

b "0" = -130.965 hartrees.

Table 4-4
Conversion from Linear To Bent SH_2(spd) Orientation(1)

	R(S-O)Å	1.08	1.58	2.07	2.57	3.07
Φ[a]	180°	1.203[a]	0.081	0.266	0.316	0.329
	175°	1.204	0.081	0.267	0.316	0.322
	160°	1.188	0.064	0.273	0.317	0.329
	144.75°	1.226	0.037	0.254	0.318	0.330
	130°	1.146	0.015	0.247	0.320	0.332
	115°	1.144	0.002	0.244	0.323	0.333
	109.5°	1.148	"0"[b]	0.243	0.324	0.335

a See footnotes in Table 4-2.

b "0" = -131.273

Table 4-5
Conversion from Linear To Bent SH_2(sp) Orientation (1)

	R(S-O)Å	1.08	1.58	2.07	2.57	3.07
Φ[a]	180°	1.629[a]	0.056	0.068	0.083	0.087
	175°	1.630	0.055	0.068	0.083	0.087
	160°	1.615	0.056	0.069	0.107	0.087
	144.75°	1.599	0.035	0.062	0.085	0.090
	130°	1.583	0.014	0.058	0.087	0.091
	115°	1.580	0.002	0.054	0.090	0.092
	109.5°	1.583	"0"[b]	0.054	0.092	0.093

a See footnotes in Table 4-2.

b "0" = -130.996

This orbital drops in energy below the antibonding Ru σ and provide a low-energy orbital (non-bonding) for the two electrons contained there.

Geometry Optimization of the O-bound Sulfoxide

The minimum calculated for the translation of the sulfide fragment relative to the Ru-oxo fragment does not correspond to the global minimum. There are degrees of freedom which have not been allowed to relax. These are mainly metal-ligand in nature and arise as a result of the change in the oxidation state of the metal. To more closely compare our results with the available experimental information,[126] a geometry optimization of all 3N-6 degrees of freedom was carried out on the minimum obtained by assuming no intra-fragment relaxation. The S-O bond changed slightly from 1.58Å to 1.54Å, as expected. This is in good agreement with the 1.56Å found experimentally for the O-bound sulfoxide in $[Ru(II)Cl_2(S\text{-}DMSO)_3(O\text{-}DMSO)]$.[126] The Ru-O bond lengthens from 1.96Å to 2.13Å, once again in good agreement with the value of 2.14Å obtained for the above compound. There was a discrepancy in the Ru-O-S angle (103.8° calcd; 120.2° exptl). However, an analysis of the isomerization of the O- to S-bound sulfoxide revealed a soft potential energy surface over a range of 50° for distortion of this angle.

Coordination-Sphere Expansion

The seven-coordinate Ru(IV) complexes of Pignolet possess sulfur ligands.[109] For the sake of completeness seven-coordinate structures were investigated. The pentagonal bipyramidal (PBP7) structure alone was studied due to the observed O-O steric interference observed for alcohols (expected to be larger for the larger sulfur atom), the greater calculated activation energy for the formation of the capped trigonal prism precursor versus the pentagonal bipyramid, 16 and 10 kcal/mole, respectively and the energetic similarity of various seven-coordinate polytopes.

The interaction studied initially was a linear (σ and π) interaction in the equatorial plane of the PBP7. The isolobal analogy[127] dictates that the removal of a ligand from a d^4, ML_7 complex will result in a vacant orbital pointing in the direction of the missing ligand. This MO corresponds to the sp^3d^3 hybrid of valence bond theory. The σ interaction will be a result of donation from the sulfide σ symmetry non-bonding MO into this vacant hybrid. The π orbitals are perpendicular in the least sterically hindered conformation and are also expected to be perpendicular as per Hoffmann's treatment of d^4, PBP7 complexes with a single faced π donor.[104]

The exclusion of the 3d AOs from the sulfur basis resulted in sulfides which are not covalently bound, R_{MS} is > 3Å at the calculated minimum. The inclusion of the 3d AOs

does not significantly increase the strength of the metal-sulfur interaction as evidenced by the nearly flat minima at 2.5Å - 2.6Å. The perturbation to a bent geometry will increase the steric repulsions.

Summary

A molecular orbital analysis of the oxidation of sulfides to sulfoxides was carried out. Direct oxygen atom transfer was found to be the most favorable. Unlike alcohol oxidation there is no energy barrier to the formation of a covalently bound substrate/oxidant species. The formation of the seven-coordinate precursors entails the expenditure of energy. The effect of the sulfur 3d AOs was investigated. The interesting result obtained was that the 3d AOs influenced the reaction in a largely electrostatic manner. The inclusion of the sulfur 3d basis decreased the dipole moment significantly by making the S-H bonds more covalent. The larger dipole moment increased the polarization of the Ru-oxo fragment, causing a destabilization for the substrate/oxidant interaction to occur at distances much larger than covalent S-O distances. Without 3d AOs the formation of covalently bounded species was not observed.

CHAPTER 5
OLEFIN OXIDATIONS BY RU-DIOXO COMPLEXES

Introduction

Since the discovery that the reaction of an Fe(III)-porphyrin with iodosyl benzene(C_6H_5-I-O) could mimic the reactivity of the O_2/Cytochrome P-450 system,[24] there has been much research on metal-oxo species.[13,128,129] Experimentally, a growing amount of work has been focused on metal-dioxo, $M(O)_2$, compounds;[41,42,130] theoretically, less attention has been paid to the electronic structure and reactivity of these complexes.[131] Griffith has derived qualitative rules for predicting which geometric isomer is the most stable as a function of d orbital population for poly-oxo complexes.[131b] Jorgensen and Hoffmann have studied the interaction of ethylene with OsO_4 using the Extended HÜckel method.[132] Rappè and Goddard have used Generalized Valence Bond calculations to study the oxidation of ethylene by various d^0 molybdenyl and chromyl species.[70,71]

Dioxo complexes are of particular interest for various reasons. First, they are plausible intermediates in the activation of O_2 by a single metal center,[130a,d] Equation 1.[86] Ru(II) species have been shown[130a,d] to regenerate the active species in the presence of O_2 without the need for

expensive and difficult to handle oxygen atom transfer reagents.[133]

$$L_nM^q + O_2 \text{ -----> } L_nM(O)_2 \qquad (1)$$

Second, there is an interesting difference in the product distributions for the cis- and trans-Ru(VI)$(O)_2$ complexes; the cis complexes[130d] lead to predominantly carbonyl products formed by the cleavage of the C=C double bond; the trans complexes[41,130a] yield epoxides as the major product. Third, many interesting pathways may be envisioned for oxidations involving these dioxo systems arising from the similarity of the cis-RuO_2 moiety with ozone.

It is the aim of the present research to get a better understanding of the Ru(VI)-dioxo/organic substrate interaction, to explore comparisons between the Ru(VI)-dioxo and Ru(IV)-oxo complexes and investigate the causes of the difference in reactivity between the cis- and trans-isomers.

Calculations

The calculations were carried out using the semi-empirical INDO/1 method.[80,81] The Restricted Open-Shell Hartree-Fock (ROHF) formalism[134] was used for open-shell species. Gradient driven geometry optimizations[97] were carried out on various structures to yield stationary points on the potential energy surface. Convergence to a minimum on the PES was assumed when the gradient was less than 5.0 x

10^{-3} hartrees/bohr. The total energy of the species converged well within 0.1 kcal $mole^{-1}$ in all cases.

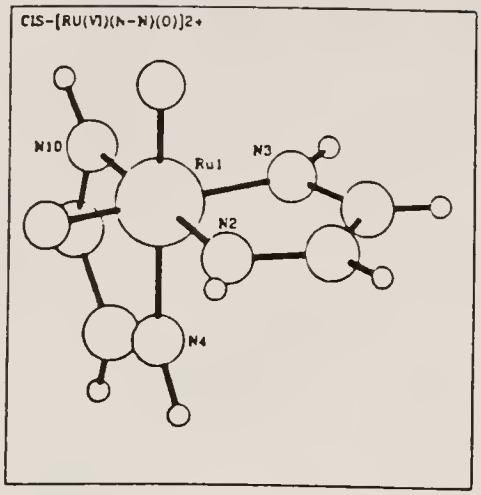
Results

Electronic Structure of Ru(VI)-dioxo complexes

The model complexes used in this present study are cis- and trans-$[Ru(VI)(NH=CH-CH=NH)_2(O)_2]^{2+}$ (hereafter referred to as cis- and trans-RuO_2^{2+}, Figure 5-1. Cis- and trans-$Ru(VI)O_2$ complexes have been used by various workers in the oxidation of different organic substrates.[41,130a,d] Optimization of the Ru-O bond lengths in the cis- and trans-complexes show the equilibrium value to lie near 1.71Å, in excellent agreement with the values of 1.718Å and 1.705Å reported by Che[98] for $Ru(VI)O_2^{2+}$ complexes with nitrogen ligands. Analogies have been made between the Ru-oxo moiety[65,74] and O_2 (with respect to the covalency of the π system and the presence of low energy singlet and triplet states[99]) then the Ru(VI)-dioxo complexes can be considered to be analogous to ozone.

The frontier orbital splitting diagrams for the cis-divacant and square planar ML_4 complexes are well known. The electronic structure of cis- and trans-dioxo complexes has also received attention in the literature.[131b] With these simple models predictions about the electronic structure of d^2 dioxo complexes have been made. There are serious deficiencies in these models, e.g. ignoring the

effects of mixing in the 5s and 5p AOs, the fact that these models are one-electron, single-determinant in nature, etc. The trans isomer is predicted to be more stable due to the lower energy of the HOMO (d_{xy}).[131b] An INDO/1 calculation places the cis isomer lower in energy than the trans by 34 kcal mol^{-1}. The reasons for this discrepancy are unclear; it may be attributed to either a deficiency in the model complex, the INDO/1 method or a single determinant representation for the ground state of the dioxo complexes. Our extensive work with INDO/1 and Ru-oxo catalyzed oxidations leads us to believe that the latter problem is the dominant factor. It is interesting to note that including electron correlation crudely (i.e. correlating the 4 highest occupied and the 4 lowest unoccupied MOs using configuration interaction - double excitations) reverses the energy ordering - the trans isomer is now lower by 35 kcal mol^{-1}. The greater correlation contribution for the trans isomer is a result of its frontier orbitals (the highest occupied and lowest unoccupied MOs have significant Ru $d\pi$ - O $p\pi$ character) being closer in energy. This leads to lower energy excited configurations and more extensive mixing. The fact that both cis- and trans-Ru(VI)O_2 and Os(VI)O_2 complexes have been described implies that the two d^2, dioxo geometries are close in energy and that factors such as steric repulsions may play an important role in determining the ground state geometry.



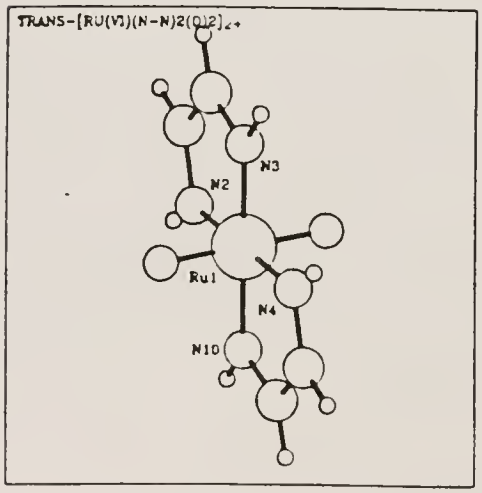


Figure 5-1: Structure of the cis- and trans-Ru(VI)$(NH{=}CH{-}CH{=}NH)_2(O)_2^{2+}$ model complexes used in the present study.

Cis-RuO_2^{2+}/Ethylene Reaction Pathways

The delocalized nature of the π bonding in the RuO_2 moiety, and the analogy with ozone, readily suggests a variety of pathways and intermediates. Three concerted pathways (and their non-concerted variants) - [1+2], [2+2] and [3+2] - were considered; they lead to the oxo/epoxide (OE), oxo/metallaoxetane (OM) and dioxometallacycle (DM) intermediates, respectively.

Geometry optimization yields weakly bound minima on the potential energy surface (PES) similar to those obtained for the Ru(IV)-oxo complexes. The average distance from the center of the C-C bond of ethylene to the center of the line which connects the two oxos is ≈ 2Å - 2.5Å. The orientation of the ethylene relative to the metal complex does not effect the strength of the binding (≈ 10 kcal mol^{-1}) as would be expected from a non-directional electrostatic interaction. The amount of electron density transferred (<0.1 electrons) is small, coming chiefly from the olefin π MO. Perturbation of either reactant from their isolated optimized geometries is insignificant. These systems differ from outer-sphere, caged-radicals in that much less than one electron is transferred. This small amount of electron density transfer keeps the double bond intact and does not lead to a loss of stereochemistry at this point in the reaction.

[1+2] Pathway

Bringing the ethylene along the concerted [1+2] pathway eventually leads to a large repulsion between the ethylene π MO and the oxo lone pair. INDO/1 calculation show that even as far out as R ≈ 2.0Å - 2.5Å moving the ethylene off the concerted [1+2] pathway leads to a lowering of the total energy by decreasing the two-orbital, four-electron repulsion between the oxo lone pair and C_2H_4 π MO. This stabilization gets larger (as a result of greater overlap and hence greater interaction) as R approaches covalent values. Deviation of the ethylene from the concerted [1+2] pathway causes it to approach the [2+2] and [3+2] pathways. At large separations there is no preference for either trajectory. Once this perturbation from the concerted [1+2] pathway is induced, formation of the oxo/epoxide can occur in a non-concerted manner. An oxo/epoxide intermediate was found, by geometry optimization, on the PES. The ground state is a singlet. The Ru-O bond lengths were 1.84Å (oxo) and 2.18Å (epoxide) consistent with experimental values of 1.77Å - 1.86Å for Ru(IV)-O complexes[98] and 2.03Å and 2.07Å for trans-$[RuCl_4(NO)(OH)]^{-2}$ and trans-$[Ru(NH_3)_4(NO(OH)]^{+2}$, respectively.[96]

[2+2] Pathway

As mentioned above, at large separations between the ethylene and cis-RuO_2 translation of the ethylene from a

[1+2] trajectory toward either a [2+2] or [3+2] pathway is equally favorable. However, as R approaches covalent values the [2+2] pathway becomes increasingly disfavored in relation to the [3+2] pathway. Simple Woodward-Hoffmann considerations state that a concerted, planar [2+2] cycloaddition is unfavorable for a 4 electron system. The Ru-O π bond, as noted above, is highly covalent. Thus, a lowering of the activation energy which causes the "forbiddeness" of the [2+2] pathway is not expected. A series of geometry optimizations along the [2+2] pathway were carried out and did not isolate an intermediate (the oxo/metallaoxetane, OM). An artificially constructed OM is not an optimized minimum on the [2+2] pathway and undergoes further geometric relaxation (and energy lowering) to arrive at a dioxometallacycle intermediate (singlet spin state).

[3+2] Pathway

A concerted [3+2] cycloaddition is an allowed reaction for a six electron system. The correlation diagram is shown in Figure 5-2. Notice the correlation of the olefin π MO with a π symmetry MO (denoted schematically by a p orbital but predominantly 4dπ in character) on the Ru. This leads to the formal two-electron reduction of the Ru(VI)-dioxo to yield the d^4 -O-Ru(IV)O-CH_2CH_2- intermediate; the bond lengths are Ru-O = 1.94Å, C-O = 1.41Å and C-C = 1.52Å.

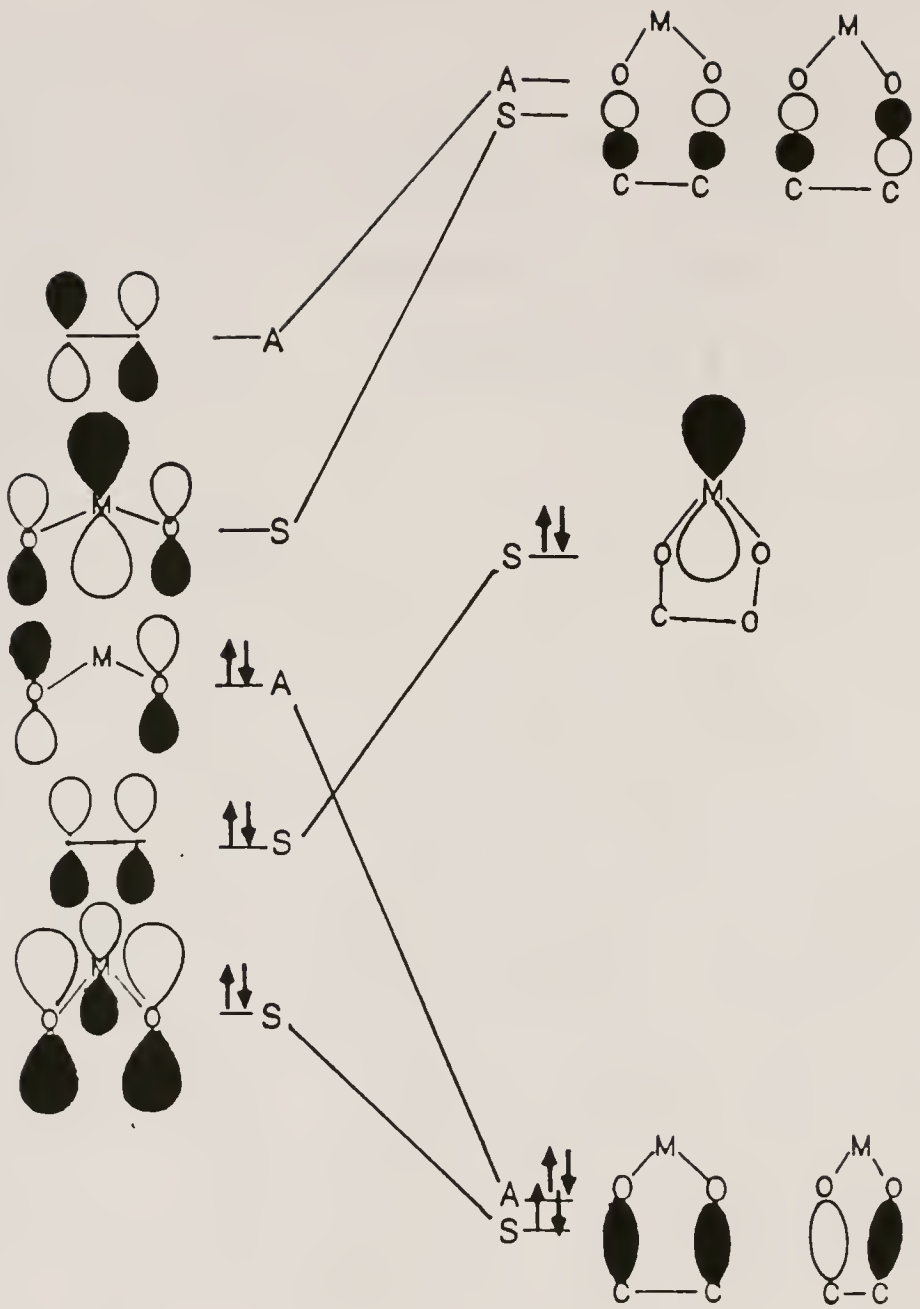


Figure 5-2: Orbital correlation diagram for the [3+2] addition (or 1,3 dipolar addition) of ethylene to a cis-RuO_2^{2+} fragment.

These values are in good agreement with the Ru-O bond distances of 2.03Å and 2.07Å quoted above for the two ruthenium-hydroxy complexes and the C-O and C-C bond lengths in tetrahydrofuran, C-O = 1.43Å±0.03Å and C-C = 1.54Å±0.02Å.[96] The O-Ru-O angle is 81°

The dioxometallacycle is roughly 90 kcal mol^{-1} lower in energy than the oxo/epoxide intermediate. As the OM does not represent a stationary point on the potential energy surface it is not possible to compare the energy of the optimized DM and OE minima with an "artificially" constructed OM. The energies of the two minima, DM and OE, can be rationalized. If the Ru-O bonds are considered to approximately cancel each other out, then the difference in energy between the DM and the OE corresponds to the difference in energy between the C-O bonds formed. In the DM two unstrained C-O bonds are formed (BE ≈ 85 kcal mol^{-1} [111]); in the OE two strained, epoxidic C-O bonds are formed (BE ≈ 50 kcal mol^{-1} [135]). Thus, a rough bond energy estimate is 70 kcal mol^{-1}, in qualitative agreement with the INDO/1 result.

The Interaction of Ethylene with trans-$[Ru(VI)(O)_2(N\text{-}N)_2]^{2+}$

The study of the trans RuO_2 species is motivated by the desire to understand the epoxidation system $Ru(TPP)(O)_2$.[130a] As with the mono oxo complex two pathways are envisioned for trans-RuO_2^{2+} - a [1+2] and [2+2] cycloaddition. It was

originally hoped that the effect of the trans ligand on stabilizing the two intermediates - bound epoxide and oxometallocycle - could be studied. However, as with every other Ru-oxo species a [2+2] "intermediate" is not a stable, stationary point on the potential energy surface. Once again, the strength of the Ru-oxo π bond should be regarded as the chief obstacle standing in the way of the [2+2] pathway. A bound epoxide intermediate is formed preferentially for the trans-$Ru(O)_2$ and trans-Ru(O)(THF) complexes. The only interesting difference between the two intermediates is the planar (with respect to the Ru-O-C-C atoms) epoxide coordination mode in the former and the non-planar coordination mode in the latter. Since the d^4 Ru(O)(bound epoxide) has a vacant $d\pi$ set, the planar coordination mode of the bound epoxide allows for maximum interaction with the epoxide π symmetry non-bonding MO. In the d^6 Ru(THF)(bound epoxide) complex both $d\pi$ orbitals are occupied and the bent coordination mode of the epoxide arises from the desire to keep the repulsive Ru $d\pi$-O$p\pi$ interaction at a minimum.

Geometric Rearrangement of cis-BE to DM

The interaction of cis-RuO_2 with ethylene yielded two distinct covalently bound minima - the oxo/epoxide (OE) and the dioxometallacycle (DM). The question arises as to whether the formation of the OE is part of competing pathway

or a "pit stop" on the way to the more stable dioxometallacycle? A look at the HOMO is informative, Figure 5-3. This HOMO may be stabilized[136] by increasing the in-phase overlap between the Ru d orbital and the O_a p orbital as well as the in-phase overlap between the C_b p orbital and O_b p orbital. To accomplish a closing of the O_b-Ru-O_a angle (i.e. an IR wagging motion) would be the simplest motion. Construction of a potential energy curve for the distortion coordinate which converts the cis-oxo/epoxide into the dioxometallacycle was carried out. The O-Ru-O angle was closed from approximately 90° while other geometric parameters were kept the same. The INDO/1 results indicate an activation barrier of roughly 6 kcal mol^{-1}. An analysis of the wavefunctions indicates a process involving the concerted breaking of one C-O bond (epoxidic) with the concomitant formation of a stronger C-O bond. Thus, it seems plausible to propose the dioxometallacycle, and the pathway leading to it, as the main route for the oxidation of olefins by a cis-Ru(VI)O_2 complex. Groves' report[135] of cis/trans epoxide isomerization by a Ru(II)-porphyrin, i.e. cist-stilbene oxide is isomerized to trans-stilbene oxide, is consistent with the notion that the bound epoxide is not "inactive" once it is formed as well as with the concept of C-O bond breaking in the bound epoxide being somewhat facile.

Discussion

The stated goals of the present research were: to get a better understanding of the metal-dioxo/organic substrate interaction, to explore comparisons between the metal-dioxo and metal-oxo complexes and investigate the causes of the difference in reactivity between the cis- and trans-isomers.

The results of this research, as with our previous study of Ru(IV)-oxo complexes, confirm that the experimental results are easily explained in simple frontier-orbital or Woodward-Hoffmann terms. The trans-dioxo complex is quite similar to the mono-oxo complex despite the change in formal oxidation state. The most favorable pathway is directly analogous to that for the mono-oxo case - a non-concerted [1+2] cycloaddition to form a Ru(IV)(O)(bound epoxide) intermediate. The lowest energy pathway for cis-RuO_2/olefin interaction is quite different - a [3+2] cycloaddition or 1,3-dipolar addition. In the cis isomer both oxygens are accessible to the same olefin and thus different pathways for olefin oxidation are encouraged as a result.

Finally, how can the difference in reactivity of the cis- and trans-Ru(VI)$(O)_2$ complexes be accounted for? The trans complex is more selective for epoxidations and is very stereospecific.[41,42,130a] The cis complex, on the other hand, leads to a large amount of cleavage products.[130d]

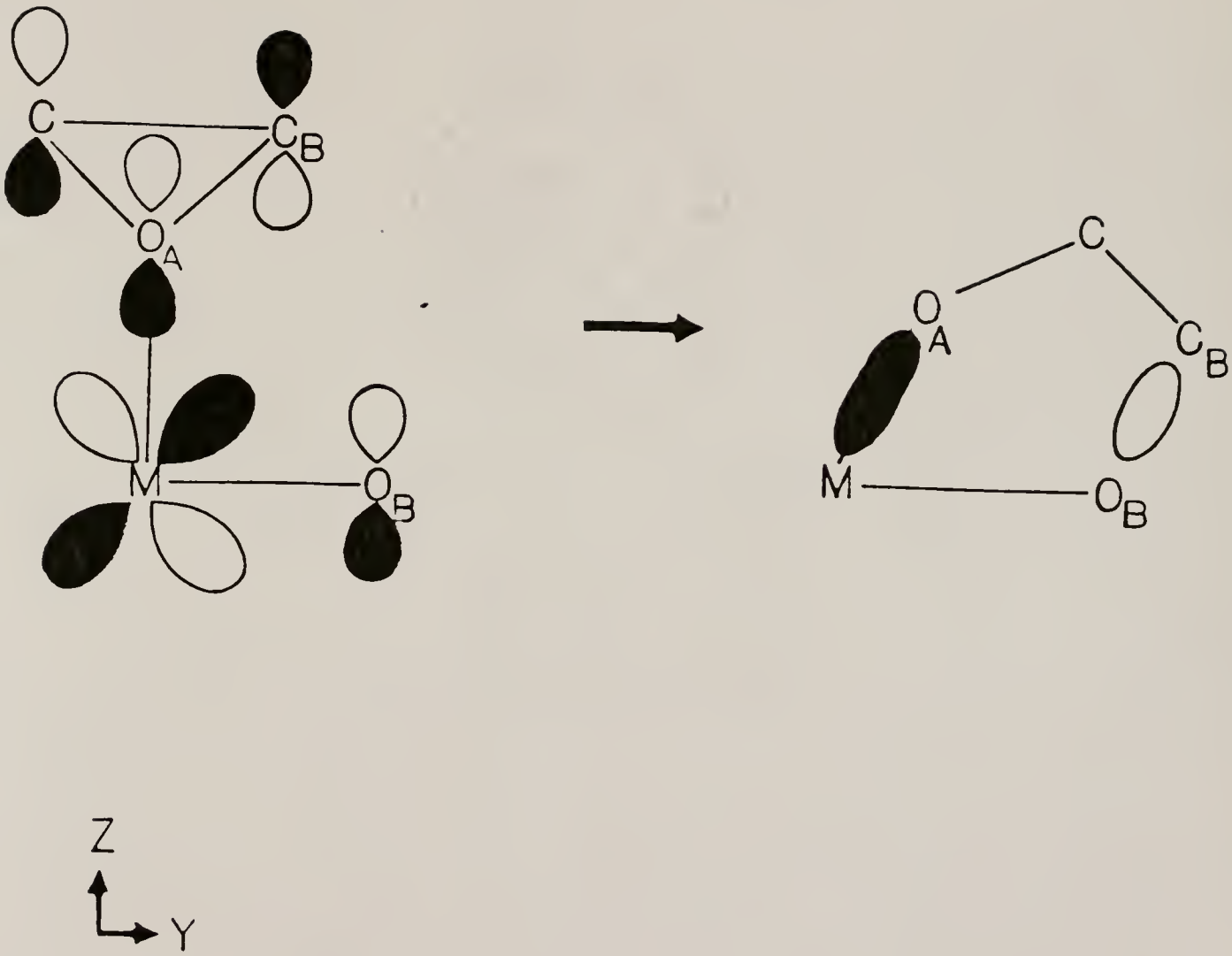


Figure 5-3: Schematic showing the composition of the HOMO of the cis-Ru-oxo/epoxide.

The larger selectivity for epoxidation pathways and high stereo-specificity for the trans isomer is consistent with the most favorable pathway being the formation of the trans-Ru(O)(epoxide) by a non-concerted [1+2] addition similar to that for Ru(IV)-oxo catalyzed epoxidations.[43] The small loss of stereochemistry which is observed is consistent with a process in which the formation of the second C-O bond is comparable to rotation about the C-C bond of the erstwhile olefin. Formation of carbonyl products by a side reaction which entails trans→cis-RuO_2 isomerization is not indicated. The theoretical analysis by Griffith[131b] points to the greater thermodynamic stability in the trans geometry for d^2 dioxo complexes. Experimental correlation for this is provided by the observation of Meyer et al. that cis-$Os(bpy)_2(O)_2^{2+}$ is unstable with respect to the trans isomer in solution.[130b]

For the cis-isomer the greater amount of carbonyl product arises from the fact that conversion of the dioxometallacycle (DM) to Ru(IV)-oxo plus epoxide is a highly endothermic process. The weak epoxidic C-O bonds allow no driving force for this pathway. The strengthening of the C-O single bonds in the DM to the double bonds of the cleavage carbonyl products is evidently sufficient enough to overcome the energy that must be spent in breaking the C-C bond of the DM. The well known cleavage of C=C double bonds by RuO_4 by way of a ruthenate ester, O_2Ru-O-CH_2-CH_2-O,

supports this view.[137] Any small amount of epoxide that results in the oxidation of olefins by cis-RuO_2^{2+} has several plausible origins. First, the higher energy cis-oxo/epoxide may be solvated or disproportionate before it can be converted into the DM. The calculated activation barrier of ≈6 kcal mol^{-1} might allow the cis-oxo/epoxide a long enough lifetime for this process to occur. Second, isomerization of the cis-RuO_2 complex to the trans isomer followed by epoxidation may occur. Finally, there may be present some partly oxidized Ru(IV)-oxo species present in solution.

CHAPTER 6
CONCLUSIONS

The theoretical results described for olefin oxidation by the six-coordinate Ru(IV)-oxo complex and the six-coordinate Ru(VI)-dioxo complexes show that these reactions can be understood in a logical manner using molecular orbital theory. Often it is thought that the "rules" of chemistry break down when transition metal species are involved. First, a charge-transfer complex, as has been proposed for epoxidations by ferryl and chromyl porphyrin systems,[31,101] is found as a minimum on the PES for $RuN_5O^{2+}\cdot C_2H_4$. Second, least motion [1+2] and [2+2] pathways are found to be unfavorable so that non-concerted processes are induced. A detailed analysis of the wavefunctions as the ethylene proceeds along these pathways reveals that the causes of the unfavorability is reminiscent of the more familiar organic analogues, i.e. the least-motion, C_{2v} addition of methylene to ethylene is analogous to the concerted [1+2] pathway and the least-motion, D_{2h} dimerization of ethylene is analogous to the concerted [2+2] pathway. Once again, as with the organic analogues non-concerted pathways may arise from the unfavorability in the concerted pathway. Perturbation of the ethylene off-center causes a dissymmetry in the C-O bonding, i.e. one C-O bond

is longer than the other, leading to a non-concerted process.

In simple chemical terms, this reaction is a nucleophilic attack of the olefin directed at the oxo oxygen. For the reasons that we have already discussed in detail the oxygen atom transfer step proceeds in a non-concerted manner, i.e. one C-O bond forms and then the second. Since this is a nucleophilic attack, a positive charge builds up on the terminal (non-bound) carbon of the substrate. Simple charge considerations lead one to predict, and INDO/1 calculations support, that $C^{\delta+}$-$O^{\delta-}$ interaction will be more favorable, and lead to bound epoxide, than $C^{\delta+}$-$Ru^{\delta+}$ interaction. The bound epoxide is a low spin, d^6 pseudo-octahedral complex and therefore, quite stable. The metal does not interact with the substrate directly but as an "electron sink" for the two electrons on being reduced from Ru(IV) to Ru(II).

The INDO/1 results show that for the oxidation of alcohols by a six-coordinate Ru(IV)-oxo complex, alcohol coordination is comparable with, if not more favorable than, a C-H activation mechanism. The linear interaction of a C-H bond in methanol with the oxo oxygen leads to a loosely bound ion-molecule interaction with a oxo-H distance of 1.2Å. The formation of a covalent oxo-H distance, corresponding to hydrogen transfer, is costly in terms of the total energy of the system for various modes. The

pentagonal bipyramid is calculated to present the best combination of favorable electronic and steric interactions. Further interaction after the seven-coordinate association complex is formed increases C-H···Oxo interaction. Thus, the preferred pathway combines both proposals, i.e. pre-coordination of the alcohol and C-H···O interaction.

This study of alcohol oxidations by a six-coordinate, high-valent metal-oxo complex with nitrogen ligands (i.e. a P-450 model) shows that when the substrate has a good donor ability direct metal participation in the oxidation pathway is plausible. Most proposed mechanisms for oxidation by P-450 models involve the metal only indirectly as a receptor for two electrons. Our results suggest that metal participation may be important; in the oxidation of substrates that possess good donor ability, i.e. alcohols, amines, and perhaps sulfides, the substrate may ligate to the metal in the course of the oxidation.

A molecular orbital analysis of the oxidation of sulfides to sulfoxides was carried out. Direct oxygen atom transfer was found to be the most favorable. Unlike alcohol oxidation there is no energy barrier to the formation of a covalently bound substrate/oxidant species.

The main goals of the Ru(VI)-dioxo/olefin research were to get a better understanding of the metal-dioxo/organic substrate interaction and to explore comparisons between the Ru-dioxo and Ru-oxo complexes and investigate the causes of

the difference in reactivity between the cis- and trans-isomers. The results of this research, as with our previous study of Ru(IV)-oxo complexes, confirm that the experimental results are easily explained in simple frontier-orbital or Woodward-Hoffmann terms. The trans-dioxo complex is quite similar to the mono-oxo complex despite the change in formal oxidation state. The lowest energy pathway for cis-RuO_2/olefin interaction is quite different - a [3+2] cycloaddition or 1,3-dipolar addition. In the cis isomer both oxygens are accessible to the same olefin and thus different pathways for olefin oxidation are encouraged as a result.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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